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Part I

POLARIMETRIC ESTIMATION OF CADMIUM

By

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ABSTRACT

Estimation of cadmium ions in aqueous solutions can be carried out quite rapidly with a fair degree of accuracy by a polarimetric method. For this purpose the cadmium ion is first converted into potassium cadmium tetra-iodide by addition of potassium iodide. Cadmium ion forms potassium cadmium tetraiodide is precipitated with the help of aqueous solution of quinine sulphate to yield an optically active complex which is isolated, dissolved and estimated polarimetrically at the room temperature. The relation of concentration of cadmium ions ($y = \text{mg}/50 \text{ ml.}$) and the optical rotation of the complex in degrees (x) can be expressed as $y = 31.62x - 2.7628$ mgs./50 ml, an expression obtained experimentally.

INTRODUCTION

It is well known that several optically active alkaloids form complexes with metallic ions and in many cases the metals in solution can be almost quantitatively precipitated by the addition of these alkaloids. Recently Liteanu and Cosma¹ have made use of such complexes in carrying out the estimation of mercury by measuring the optical rotation of the complex formed by quinine with potassium-iodo-mercurate. They measured optical rotation of different concentrations of solutions, containing Hg^{2+} ions by first converting it into tetra-iodo-mercurate with the help of potassium iodide and then precipitating with quinine-mono-chlorohydrate solution. The properly washed precipitate was dissolved in acetone and solution thus obtained was subjected to polarimetric measurement at the room temperature. A plot of rotation against concentration showed a straight line from which a relationship $y = -7.1 + 1.433x = \text{mg. Hg}/100 \text{ ml}$, where $x =$ angle of rotation expressed in $1/100^\circ$, could be deduced. In the present paper the authors have described polarimetric estimation of cadmium ions by a similar method.

EXPERIMENTAL

Martini² has used quinine sulphate for the micro-chemical detection of small quantities of cadmium and found that it could detect one part of cadmium chloride in two hundred parts of solution. Korenman³ used free base in conjunction with potassium iodide for the detection of cadmium and found the sensitivity of the reaction was 1:600,000. Authors, therefore, decided to use quinine sulphate with potassium iodide to precipitate Cd^{++} anion in the form of an optically active complex.

The estimations were carried out by using different amounts of cadmium sulphate solutions containing 2.5 gms in 250 ml. The volume of solution taken for different estimations was from 1 ml. to 50 ml, corresponding to 4.4034 mgs to 220.17 mgs of cadmium anion. To each of these solutions was added 80 ml. of potassium iodide solution (40 gms per litre). To this solution was added an excess of 1.2 % solution of quinine sulphate. A white precipitate of the complex was obtained which was filtered and washed with a little petroleum ether. The precipitate was then dissolved in acetone and the volume was made upto 50 ml. Polarimetric measurements were carried out with this solution, using a two decimeter tube at room temperature (15-16°C).

To check the amount of cadmium anions in the solution, a separate sample of original solution was gravimetrically estimated as cadmium quinaldinate.⁴

In table 1 are given the values of optical rotation for different amounts of cadmium anions, present in solution of cadmium sulphate taken.

TABLE 1
Optical rotation of solutions containing different amount of Cd^{++} in the form of optically active complex

	$\text{Cd}^{++}/50 \text{ ml.}$ (mg)	Optical rotation in degrees For Hg5461
1.	4.4034	.18
2.	11.0085	.46
3.	22.0170	.86
4.	44.034	1.73
5.	66.051	2.10
6.	77.0595	2.60
7.	83.068	2.88
8.	143.1105	4.71
9.	154.119	4.90
10.	176.136	5.53
11.	198.153	6.42
12.	220.170	7.16

DISCUSSION

A plot of concentration against observed optical rotation shows a linear relationship (Fig. 1)

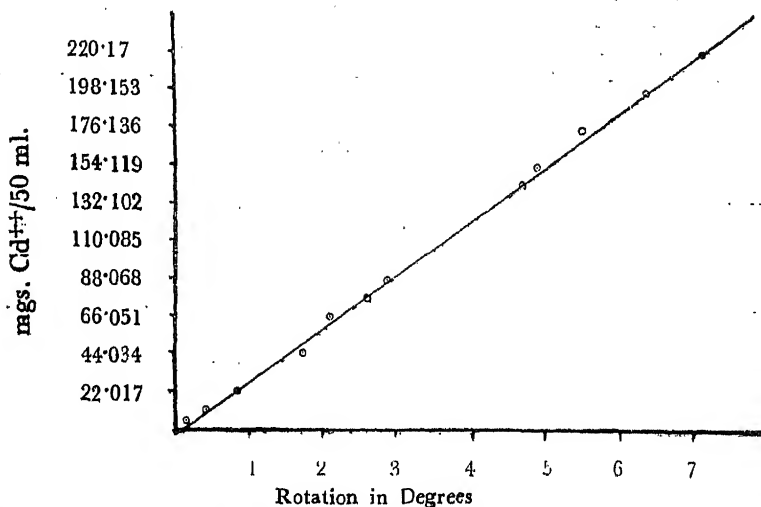


Fig. 1. Graph showing relationship between optical rotation and concentration.

The equation of the curve was calculated by the method of least squares and the following expression was obtained.

$$y = 31.62x - 2.7628 \text{ mgs Cd}^{++}/50 \text{ ml.}$$

where x is the angle of rotation in degrees and y is the concentration of Cd^{++} in mg/50 ml.

In Table 2 a comparison is made between the estimated value of cadmium ions and the value obtained from empirical equation, given above, for different volumes of solution.

TABLE 2

Comparison of the amount of Cd^{++} present in different volumes of solution by gravimetric estimation and polarimetric estimation

S. N.	volume of cadmium-sulphate solution (ml)	Amount of cadmium (mg)		Difference (a)-(b) (mg)
		(a) gravimetric estimation	(b) Polarimetric estimation	
1.	1	4.4034	2.9288	+1.5
2.	2.5	11.0085	11.7824	-.8
3.	5	22.017	24.4304	-2.4
4.	10	44.034	41.9398	+2.1
5.	15	66.051	63.6392	+2.4
6.	17.5	77.0595	79.4492	-2.3
7.	20	88.068	88.3028	-0.2
8.	32.5	143.1105	146.1674	-3.0
9.	35	154.119	152.175	+1.9
10.	40	176.136	172.0958	+4.0
11.	45	198.153	200.2376	-2.1
12.	50	220.170	223.6364	-3.4

It is clear from Table 2 that polarimetric estimation of cadmium ions gives fairly accurate results even in quite low concentrations of cadmium ions in solution. It is also apparent that higher the concentration of cadmium ions in solution, the greater is the accuracy of the polarimetric estimation. The method is apparently not very suitable for direct estimation of solutions containing less than 0.008 % of cadmium ions. In all such cases, however, the solution can be concentrated and the polarimetric estimations can be carried out with fair degree of accuracy.

CONCLUSION

Cadmium ions in aqueous solutions can be estimated with a fair degree of accuracy quite rapidly polarimetrically. For this purposes potassium iodide is added to solution of cadmium salt to form potassium cadmium tetra-iodide which can be precipitated with aqueous solution of quinine sulphate. Cadmium is thus obtained in the form of optically active complex. This can be dissolved in acetone and estimation of cadmium ions can be carried out quite rapidly polarimetrically with the help of empirical equation, obtained experimentally.

ACKNOWLEDGEMENTS

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REFERENCES

1. Liteanu, C. and Cosma, M., *Talanta*, **8**, 313 (1961).
2. Martini, A., *Anales asoc. quim., Argentina*, **14**, 177 (1926) ; **15**, 52 (1927) ; *Mikrochemie*, **6**, 1 (1927).
3. Korenman, I. M., *Z anal. chem.*, **99**, 402 (1934) ; *Farm. Zhur.*, **7**, 98 (1934).
4. Vogel, I. *Quantitative Inorganic Analysis*, Second Edition, Longmans, p. 429.

SOME THEOREMS ON A GENERALISED HANKEL TRANSFORM

By

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ABSTRACT

Mehra (2) has recently given a generalisation of the Hankel transform by means of an integral equation

$$g(x) = \left(\frac{1}{2}\right)^v \int_0^\infty (xy)^{v+\frac{1}{2}} \chi_{v,k+\frac{1}{2},m} \left(\frac{1}{2} x^2 y^2\right) f(y) dy.$$

In this paper two Theorems, with their various particular cases have been given. These theorems give kernels connecting different classes of self-reciprocal functions. I have given the proof of Theorem 1 in detail and the proof of other Theorems follow the same line as Theorem 1.

1. Mehra [2] has recently introduced a generalisation of the Hankel-transform

$$g(x) = \int_0^\infty \sqrt{xy} J_v(xy) f(y) dy, \quad (1.1)$$

by means of an integral equation

$$g(x) = 2^{-v} \int_0^\infty (xy)^{v+\frac{1}{2}} \chi_{v,k+\frac{1}{2},m} \left(\frac{x^2 y^2}{4}\right) f(y) dy, \quad (1.2)$$

where

$$\begin{aligned} \chi_{v,k+\frac{1}{2},m}(x) &= \sum_{m,-m} \frac{\Gamma(2m) \Gamma(v+1-m-3k)}{\Gamma(m-k) \Gamma_x(v+1-m-2k \pm m)} x^{k-m} \times \\ &\times {}_2F_3 \left[\begin{matrix} 1+k-m, v+1-m-3k \\ 1-2m, v+1-m-2k \pm m \end{matrix} ; -x \right] \end{aligned} \quad (1.3)$$

Theorem A :—A necessary and sufficient condition that a function of $A(\alpha, a)$ be $R_{v(k+\frac{1}{2},m)}$ is that it should be of the form

$$f(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^{s/2} \Gamma_x(v/2+s/2+\frac{1}{2} \pm m-k)}{\Gamma(v/2+s/2+\frac{1}{2} - 2k)} \psi(s) x^{-s} ds, \quad (1.4)$$

here $\psi(s)$ is regular and satisfies the functional relation $\psi(s) = \psi(1-s)$ (1.5)

in the strip $a < \sigma < 1-a$. (1.6)

for every positive η and uniformly in any strip interior to (1.6) and c is any value of σ satisfying (1.6).

2. Theorem 1.

If

$$k(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^s \Gamma_x(v/2+s/2+\frac{1}{2}-k\pm m) \Gamma_x(\mu/2+s/2+\frac{1}{2}-l\pm n)}{\Gamma(v/2+s/2+\frac{1}{2}-2k) \Gamma(\mu/2+s/2+\frac{1}{2}-2l)} \omega(s) x^{-s} ds. \quad (2.1)$$

where $\omega(s)$ satisfies (1.5) in the strip (1.6)

$$\text{and } f(x) = \frac{1}{2\pi i} \int_{c'-i\infty}^{c'+i\infty} \frac{2^{s/2} \Gamma_x(v/2+s/2+\frac{1}{2}-k\pm m) \Gamma_x(\mu/2+s/2+\frac{1}{2}-l\pm n)}{\Gamma(v/2+s/2+\frac{1}{2}-2k) \Gamma(\mu/2+s/2+\frac{1}{2}-2l)} \times \\ \frac{\Gamma_x(\lambda/2-s/2+\frac{3}{2}-p\pm q)}{\Gamma(\lambda/2+s/2+\frac{3}{2}-2p)} \phi(s) x^{-s} ds. \quad (2.2)$$

where $\phi(s)$ satisfies (1.5) in the strip (1.6) and

$$\phi(s) = O\left(e^{(\frac{3}{2}\pi - \alpha + \eta)|t|}\right),$$

then the function,

$$g(x) = \int_0^\infty f(y) k(xy) dy \quad (2.3)$$

is $R_{\lambda(p+\frac{1}{2}, q)}$ and belongs to the class $A(3\alpha, a)$.

Proof:— We have

$$g(x) = \frac{1}{2\pi i} \int_0^\infty f(y) dy \int_{c-i\infty}^{c+i\infty} \frac{2^s \Gamma_x(v/2+s/2+\frac{1}{2}-k\pm m) \Gamma_x(\mu/2+s/2+\frac{1}{2}-l\pm n)}{\Gamma(v/2+s/2+\frac{1}{2}-2k) \Gamma(\mu/2+s/2+\frac{1}{2}-2l)} \\ \omega(s) (xy)^{-s} ds. \quad (2.4)$$

Changing the order of integration, which is permissible, we get,

$$g(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^s \Gamma_x(v/2+s/2+\frac{1}{2}-k\pm m) \Gamma_x(\mu/2+s/2+\frac{1}{2}-l\pm n)}{\Gamma(v/2+s/2+\frac{1}{2}-2k) \Gamma(\mu/2+s/2+\frac{1}{2}-2l)} \\ \omega(s) x^{-s} \int_0^\infty y^{-s} f(y) dy. \quad (2.5)$$

Therefore, by Mellin's Inversion formula, we have

$$g(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^s \Gamma_x(v/2+s/2+\frac{1}{4}-k\pm m) \Gamma_x(\mu/2+s/2+\frac{1}{4}-l\pm n)}{\Gamma(v/2+s/2+\frac{1}{4}-2k) \Gamma(\mu/2+s/2+\frac{1}{4}-2l)} \omega(s) x^{-s} \times$$

$$\frac{2^{\frac{1}{2}-s/2} \Gamma_x(v/2-s/2+\frac{3}{4}-k\pm m) \Gamma_x(\mu/2-s/2+\frac{3}{4}-l\pm n) \Gamma_x(\lambda/2+s/2+\frac{1}{4}-p\pm q)}{\Gamma(v/2-s/2+\frac{3}{4}-2k) \Gamma(\mu/2-s/2+\frac{3}{4}-2l) \Gamma(\lambda/2+s/2+\frac{1}{4}-2p)} \phi(s) x^{-s} ds. \quad (2.6)$$

$$\text{i. e. } g(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^{s/2} \Gamma_x(\lambda/2+s/2+\frac{1}{4}-p\pm q)}{\Gamma(\lambda/2+s/2+\frac{1}{4}-2p)} \psi(s) x^{-s} ds.$$

where

$$\psi(s) = \frac{2^{\frac{1}{2}} \Gamma_x(v/2+s/2+\frac{1}{4}-k\pm m) \Gamma_x(\mu/2+s/2+\frac{1}{4}-l\pm n) \Gamma_x(v/2-s/2+\frac{3}{4}-k\pm m)}{\Gamma(v/2+s/2+\frac{1}{4}-2k) \Gamma(\mu/2+s/2+\frac{1}{4}-2l) \Gamma(v/2-s/2+\frac{3}{4}-2k)} \times$$

$$\times \frac{\Gamma_x(\mu/2-s/2+\frac{3}{4}-l\pm m)}{\Gamma(\mu/2-s/2+\frac{3}{4}-2l)} \omega(s) \phi(s)$$

Thus $\psi(s)$ satisfies (1.5) and hence $g(x)$ is $R_{\lambda}(p+\frac{1}{2}, q)$.

It only remains to justify the inversion of the order of integration in (2.5). Putting $s = c+it$ and applying the asymptotic formula

$$|\Gamma(A+\frac{1}{2}it)| \sim C e^{-\pi/4|t|} |t|^{A-\frac{1}{2}}$$

to the integral (2.5) we see that it is not greater than a constant multiple of

$$x^{-c} \int_{-\infty}^{\infty} e^{-\pi/2|t|} |t|^{\frac{1}{2}(\mu+\nu)+c-\frac{1}{2}} \omega(c+it) dt \int_0^{\infty} y^{-c} |f(y)| dy.$$

The change in the order of integration will thus be permitted if both the y - and the t -integrals exist.

Now since $\omega(s) = O(e^{(\pi/2-2\alpha+2\eta)|t|})$, the t -integral

is of order $e^{(2\eta-2\alpha)|t|} |t|^{\frac{1}{2}(\mu+\nu-1)+c}$,

and therefore, the integral exists if $R(\alpha-\eta) > 0$,

$$N. B. \quad \Gamma_x(\alpha\pm\beta) = \Gamma(\alpha+\beta) \Gamma(\alpha-\beta).$$

The convergence of the γ -integral follows from the definition of $f(x)$ and hence the change in the order of integration is justified.

Particular Cases :—The following are a few interesting particular cases of the above stated theorem.

Case (i). Putting $\lambda = \mu$, $p = l$ and $q = n$, we get a theorem due to Mehra (2).

If $f(x)$ is $R_{\nu(k+\frac{1}{2}, m)}$ and

$$k(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^s \Gamma_x(\nu/2+s/2+\frac{1}{4}-k\pm m) \Gamma_x(\mu/2+s/2+\frac{1}{4}-l\pm n)}{\Gamma(\nu/2+s/2+\frac{1}{4}-2k) \Gamma(\mu/2+s/2+\frac{1}{4}-2l)} \omega(s) x^{-s} ds,$$

$$\text{then } g(x) = \int_0^\infty k(xy) f(y) dy, \text{ is } R_{\mu(l+\frac{1}{2}, n)}.$$

Case II. If $p = -q$ we get :

Theorem 2 : If

$$k(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^s \Gamma_x(\nu/2+s/2+\frac{1}{4}-k\pm m) \Gamma_x(\mu/2+s/2+\frac{1}{4}-l\pm n)}{\Gamma(\nu/2+s/2+\frac{1}{4}-2k) \Gamma(\mu/2+s/2+\frac{1}{4}-2l)} \omega(s) x^{-s} ds,$$

where $\omega(s)$ satisfies (1.5).

$$\text{and } f(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^{s/2} \Gamma_x(\nu/2+s/2+\frac{1}{4}-k+m) \Gamma_x(\mu/2+s/2+\frac{1}{4}-l\pm m)}{\Gamma(\nu/2+s/2+\frac{1}{4}-2k) \Gamma(\mu/2+s/2+\frac{1}{4}-2l)} \phi(s) x^{-s} ds,$$

$$\text{where } \phi(s) \text{ satisfies (1.5), then the function given by}$$

$$g(x) = \int_0^\infty k(xy) f(y) dy$$

is R_λ i. e. $g(x)$ is Self-Reciprocal function for the Hankel transform of order λ .

Case III. Taking $k = -m$, in addition to $p = -q$, we obtain,

Theorem 3. If

$$k(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{2^s \Gamma_x(\nu/2+s/2+\frac{1}{4}) \Gamma_x(\mu/2+s/2+\frac{1}{4}-l\pm n)}{\Gamma(\mu/2+s/2+\frac{1}{4}-2l)} \omega(s) x^{-s} ds,$$

$$\text{and } f(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^{s/2} \frac{\Gamma(v/2+s/2+\frac{1}{4}) \Gamma_x(\mu/2+s/2+\frac{1}{4}-l\pm n) \Gamma(\frac{3}{2}+\lambda/2-s/2)}{\Gamma(\mu/2+s/2+\frac{1}{4}-2k)} \times \\ \times \phi(s) x^{-s} ds$$

where $\phi(s)$ and $\omega(s)$ satisfies (1.5) then the function

$$g(x) = \int_0^\infty k(xy) f(y) dy,$$

is one that belongs to the class R_λ .

Case IV. Finally taking, $n = -l$, $k = -m$, $p = -q$, we obtain a result due to Brij Mohan namely, if

$$k(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^s \Gamma(\frac{1}{2}+v/2+s/2) \Gamma(\frac{1}{2}+\mu/2+s/2) \omega(s) x^{-s} ds,$$

$$\text{and } f(x) = \frac{1}{2\pi i} \int_{k-i\infty}^{k+i\infty} 2^{s/2} \Gamma(\frac{1}{2}+\mu/2+s/2) \Gamma(\frac{1}{2}+v/2+s/2) \Gamma(\frac{3}{2}+\lambda/2-s/2) \times \\ \times \phi(s) x^{-s} ds,$$

then the function

$$g(x) = \int_0^\infty k(xy) f(y) dy,$$

is R_λ

4. Theorem 4 :—If

$$k(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{\Gamma_x(\frac{1}{2}+v/2+s/2-k\pm m) \Gamma_x(\mu/2+\frac{3}{4}-\frac{1}{2}s-l\pm n)}{\Gamma(v/2+s/2+\frac{1}{4}-2k) \Gamma(\mu/2-s/2+\frac{3}{4}-2l)} \omega(s) x^{-s} ds.$$

where $\omega(s)$ satisfies (1.5)

and

$$f(x) = \frac{1}{2\pi i} \int_{k-i\infty}^{k+i\infty} 2^{s/2} \frac{\Gamma_x(v/2+s/2+\frac{1}{4}-k\pm m) \Gamma_x(\mu/2+\frac{3}{4}-s/2-l\pm n)}{\Gamma(v/2+s/2+\frac{1}{4}-2k) \Gamma(\mu/2+\frac{3}{4}-s/2-2l)} \times \\ \times \frac{\Gamma_x(\lambda/2+s/2+\frac{1}{4}-p\pm q)}{\Gamma(\lambda/2+s/2+\frac{1}{4}-2p)} \phi(s) x^{-s} ds.$$

where $\phi(s)$ satisfies (1.5) then the function

$$g(x) = \int_0^{\infty} k(y) f(xy) dy$$

is one that belongs to $R_{\lambda}(p \pm \frac{1}{2}, q)$.

The proof is similar to that of Theorem 1. As in the previous theorem, the foregoing theorem is also capable of yielding several results as its particular case. If we assume $p=l$, $q=n$ and $\lambda=\mu$, we get a result due to Mehra [2].

5. Theorem 5 and 6 :

Theorem 1 and 4 also hold good if the functions $\omega(s)$ and $\phi(s)$ satisfy the functional relation

$$\phi(s) = -\phi(1-s), \text{ in place of (1.5).}$$

6. Theorem 7 and 8 :

If either of the functions $\omega(s)$ or $\phi(s)$ satisfies the relation (1.5) where as the other satisfies the relation $\phi(s) = -\phi(1-s)$,

then, in both the cases the function $g(x)$ is $-R_{\lambda}$,

The author wishes to express his respectful thanks to Dr. Brij Mohan for his kind help and suggestions in the preparation of this note.

REFERENCES

1. A. Erdelyi, Higher Transcendental functions Vol. 1 (1953).
2. A. N. Mehra, Thesis approved for the Ph. D. Degree by Lucknow University (1958).
3. Brij Mohan, *Proc. Physico. Math. Soc. Japan*, **16**, 273 (1938).
4. Brij Mohan, *Quart Journal of Maths.* (Oxf. Series) **10**, 252 (1939).

ON THE KAMKE'S FUNCTION IN THE UNIQUENESS THEOREM OF ORDINARY DIFFERENTIAL EQUATIONS

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ABSTRACT

In this paper, we define a Kamke's function and obtain sufficient conditions for a function to be a Kamke's function. We show that when certain conditions of Kamke's uniqueness theorem are violated, the solution is non-unique. We also observe that the monotonic restriction on Kamke's function in the convergence of successive approximations results, is not quite necessary.

Let y and f be vectors with n real components and let $f = f(x, y)$ be a continuous function on $0 \leq x < a$ and $|y| < b$. Then there exists on some interval $0 \leq x \leq a_0$ ($\leq a$) on which the initial value problem

$$(1) \quad y' = f(x, y), \quad y(0) = 0$$

has at least one solution. (Peano).

We shall say that a function $h(x, r)$ is a Kamke's function if $h(x, r) \geq 0$ is a continuous function on $0 < x < a, r \geq 0$ having the following property:—

the only solution $r(x)$ of the differential equation

$$(2) \quad r' = h(x, r)$$

which exists for $0 < x < \alpha \leq a$ and satisfies both the limiting conditions

$$(3) \quad r(x) \rightarrow 0, \quad x \rightarrow 0; \quad r'(x) \rightarrow 0, \quad x \rightarrow 0.$$

is the function $r(x) \equiv 0$. Then the well known general uniqueness theorem is as follows: (C.F.[1])

THEOREM: Suppose $h(x, r)$ is a Kamke's function and $f(x, y)$ satisfies the inequality,

$$(4) \quad |f(x, y_1) - f(x, y_2)| \leq h(x, |y_1 - y_2|).$$

Then there is a unique solution of (1) through $(0, 0)$.

It is also known [2] and [3] that successive approximations coverage if, in addition, $h(x, r)$ is non-decreasing in r .

The object of this note is to find sufficient conditions for a function to be Kamke's function and to show that the additional restriction of monotony is not quite necessary. Incidentally we prove that two different solutions can be constructed when certain conditions of uniqueness theorem are violated. This will, of course, be a generalisation of a non-uniqueness result in [4].

2. Defining a Kamke's functions as above, the following result can immediately be noted which will be used in theorem II.

THEOREM I. If $h(x, r)$ is a Kamke's function and if

$$(5) \quad 0 \leq g(x, r) \leq h(x, r)$$

where $g(x, r)$ is continuous on $0 < x < a, r \geq 0$, then $g(x, r)$ is also a Kamke's function.

PROOF: Suppose $h(x, r)$ is a Kamke's function. Then according to Kamke's general uniqueness theorem, $r(x) \equiv 0$ is the only integral of the differential equation (2) having the property (3). Since equation (2) is having an identically zero solution clearly the differential equation

$$(6) \quad r' = g(x, r)$$

has the same solution. Further we must show that all solutions $r(x) \equiv 0$ of (6) are such that they violate the limiting properties (3).

Suppose, on the contrary, that there is a solution $r(x) \equiv 0$ of (6) satisfying the conditions (3). Then consider any solution of $r' = h(x, r) + \epsilon$, where ϵ is an arbitrarily small positive quantity, through $\{x_0, r(x_0)\}$ where $r(x_0) > 0$. Let such a solution be $k(x, \epsilon)$. It is easy to show that

$$(7) \quad r(x) \geq k(x, \epsilon) \quad \text{for } 0 < x \leq x_0.$$

For suppose that this relation does not hold. Then, without loss of generality, let $[x_1, x_0]$ be an interval where $r(x) \leq k(x, \epsilon)$. At x_0 , we have $r(x_0) = k(x_0, \epsilon)$. Hence by taking left hand derivatives at x_0 , we obtain the inequality

$$(8) \quad r'(x_0) \geq k'(x_0, \epsilon)$$

From this we obtain a further inequality

$$(9) \quad g(x_0, r(x_0)) \geq h(x_0, k(x_0, \epsilon)) + \epsilon$$

which leads to a contradiction. Hence (7) holds. Since we know that $\lim_{\epsilon \rightarrow 0} k(x, \epsilon)$

$= b(x)$, where $b(x)$ is the maximal solution of (2) through $\{x_0, r(x_0)\}$, we obtain from (7)

$$(10) \quad 0 \leq b(x) \leq r(x) \quad \text{for } 0 < x \leq x_0.$$

By assumption $r(x)$ satisfies the conditions (3), Hence $b(x) \equiv 0$, which is a solution of (2), has the properties (3) which is a contradiction to the hypothesis. Hence $g(x, r)$ is a Kamke's function.

THEOREM II. Suppose $L(x) \geq 0$ is a continuous function on $0 < x \leq a$. Let the function $h(x, r)$ satisfy the condition

$$(11) \quad h(x, r) \leq L(x) r;$$

Suppose further

$$(12) \quad \limsup_{x \rightarrow 0} [1 + L(x)] e^{-p(x)} > 0 \text{ where}$$

$$(13) \quad p(x) = \int_x^{x_0} L(s) ds \quad (x \neq 0);$$

then $h(x, r)$ is Kamke's function.

PROOF: Consider the differential equation

$$(14) \quad r' = L(x) r.$$

The solution $r(x) \equiv 0$ of (14) are non-vanishing constant multiples of the function $e^{-p(x)}$, where $p(x)$ is given by (13). The derivative of this function is

$L(x) \neq 0$. Since $L(x) \geq 0$, it follows from the assumption (12) that every solution $r(x) \equiv 0$ of (14) violates one, at least, of the two limiting conditions (3). Hence the function $L(x)r$ is a Kamke's function.

Since the condition (11) is satisfied Theorem I gives the result immediately.

Now we shall consider the non-uniqueness result. This is true when the differential equation (1) is of first order.

THEOREM III. Let $h(x, r) > 0$ be continuous on $0 < x < a, r > 0$ and $h(x, 0) \equiv 0$; Suppose for each $\alpha, 0 < \alpha < a, k(x) > 0$ is a differentiable function on $0 < x < \alpha$ which satisfies

$$(15) \quad k'(x) = h(x, k(x)) \quad \text{on } 0 < x < \alpha$$

and such that $k'(0)$ exists and

$$(16) \quad k(0) = k'(0) = 0.$$

Suppose further the function $f(x, y)$ of the differential equation (1) satisfies the condition

$$(17) \quad |f(x, y_1) - f(x, y_2)| \geq h(|x|, |y_1 - y_2|)$$

Then the differential equation (1) has at least two solutions passing through $(0, 0)$.

PROOF: First suppose that for $y = 0$

$$(18) \quad f(x, 0) \equiv 0 \quad \text{in } |x| < a.$$

In the inequality (17), write $y_2 = y$ and $y_1 = 0$. We get

$$(19) \quad |f(x, y)| \geq h(|x|, |y|)$$

It is enough to consider the theorem in the first quadrant for the proof in the other quadrants is similar. Since $f(x, y)$ is continuous and $h(x, r) > 0$ the inequality (17) shows that for ordinates different from zero, $f(x, y) \leq 0$ in each single quadrant which implies either

$$(20) \quad f(x, y) \geq h(x, y)$$

Or

$$(21) \quad f(x, y) \leq -h(x, |y|) \quad \text{for } 0 < x < a, y > 0.$$

We shall consider the case (20) first. The proof of the other case (21) is similar.

Let $y(x, \epsilon)$ be a solution of $y' = f(x, y) + \epsilon$ through $(x_0, k(x_0))$ where $k(x_0) > 0$, ϵ is an arbitrarily small positive quantity and x_0 is any point in $0 < x < a$.

By similar reasoning employed in Theorem I it is easy to show that $y(x) = \lim_{\epsilon \rightarrow 0} y(x, \epsilon) \leq k(x)$ for $0 < x \leq x_0$, where $y(x)$ is a solution of (1).

One can always find a solution $y(x)$ of (1) which is non-negative in $0 < x \leq x_0$. For, if $y(x)$ is negative in $0 < x < x_1 < x_0$, then we can select that portion of $y(x)$ lying between x_1 to x_0 and combine it with $y \equiv 0$ in $0 < x < x_1$. That this newly formed curve, say $y_1(x)$, is also a solution of (1) through $(x_0, k(x_0))$, is obvious from (18). These considerations show that

$$0 \leq y(x) \leq k(x) \quad \text{for } 0 < x \leq x_0.$$

Since by hypothesis $k(O) = k'(O) = O$, it follows that $y(O) = y'(O) = O$ which implies that $y(x)$ is a solution of (1) passing through (O, O) . This proves that the differential equation (1) has a solution different from zero passing through (O, O) .

On the other hand, as the equation (18) holds, differential equation (1) admits an integral curve y passing through (O, O) which is identically zero. Hence, one has two different solutions through (O, O) .

Finally, we, can remove the restriction (18). Let $y = y_0$ be one solution. Then consider $z = y - y_0$ where y is another solution. Then

$$(22) \quad \begin{aligned} z' &= y' - y_0' = f(x, y) - f(x, y_0) = f(x, z + y_0) - f(x, y_0) \\ &= F(x, z), \text{ (say.)} \end{aligned}$$

Now $F(x, O) = f(x, y_0) - f(x, y_0) = O$ for all x . It follows therefore that z is identically zero is one solution of $z' = F(x, z)$ through (O, O) . But (22) has a solution different from zero. This implies that y is not identically equal to y_0 . Hence the differential equation (1) has more than one solutions through (O, O) which proves the theorem.

As noted above the convergence of successive approximations has been proved with the additional restriction of monotony on Kamke's function $h(x, r)$ in [2], [3]. That the monotonic restriction is not quite necessary is seen from the

THEOREM IV : Suppose that the condition (4) is replaced by

$$(23) \quad |f(x, y_1) - f(x, y_2)| \leq g(x, |y_1 - y_2|) \leq h(x, |y_1 - y_2|)$$

where $g(x, r)$ is continuous and non-decreasing in r . Then the successive approximations of the differential equation (1) converge.

An application of theorem I shows that $g(x, r)$ is a Kamke's function on account of (23). Since it is also monotonic, the result follows from [2] or [3]. This suggests that the additional monotonic restriction becomes superfluous if the condition (4) of the uniqueness theorem is replaced by

$$(24) \quad \begin{aligned} \text{Max } |F(x, y_1 - y_2)| &\leq h(x, r), \\ 0 &\leq |y_1 - y_2| \leq r \end{aligned}$$

where $|f(x, y_1) - f(x, y_2)| \leq |F(x, y_1 - y_2)|$.

For, if we put $g(x, r) = \text{Max } |F(x, y_1 - y_2)|$, then the

$$0 \leq |y_1 - y_2| \leq r$$

situation is same as in theorem IV, since (24) means

$$(25) \quad |f(x, y_1) - f(x, y_2)| \leq g(x, r) \leq h(x, r).$$

REFERENCES

1. Kamke, E., Differential Gleichungen roller functionen, Leipzig (1930).
2. Coddington and Levinson, Uniqueness and Covergence of Successive Approximations. *Ind. Jr. Maths.* (1952).
3. Viswanthan, B., The general uniqueness theorem and the convergence of successive approximations. *Ind. Jr. Maths.* (1952).
4. Tamarkine, J., Sur le theoreme d'unicite des solutions des equations differentielle ordinaries. *Math. Zeit.* (1952).

BENTONITE AS GROWTH MEDIUM FOR NITRITE FORMING BACTERIA (NITROSOMONAS) : PART II

By

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ABSTRACT

Nitrosification in bentonite medium has been studied in the presence of magnesium, calcium, strontium and barium carbonates. Magnesium carbonate as well as calcium carbonate both have been observed to stimulate the process equally. Strontium and barium carbonates are not favourable for the process. To obtain as good results as with Omeliansky's medium, the ratio between the amounts of magnesium or calcium carbonate and bentonite, that should be maintained in bentonite medium is found to be 1:20.

In a previous communication (1), we reported the results obtained on the extent of nitrite formation as related to the growth of nitrosomonas in bentonite medium and also in the presence of magnesium and calcium carbonates. It was observed that bentonite without any optimum amounts of free calcium and magnesium carbonates is not a good medium for nitrosification and that in the presence of 50 mg of free magnesium carbonate, the process advanced better than in the corresponding medium which contained calcium carbonate. In that medium, the growth of nitrosomonas as related to the amount of nitrite formed was comparable with the results obtained in Omeliansky's medium. The experiments were performed with 1g. of bentonite.

We have performed similar experiments with 1.5 g. and 2.0 g. of bentonite and in the presence of two additional carbonate samples *viz.*, carbonates of barium and strontium.

EXPERIMENTAL

Details of the procedure have already been described in our previous communication (1). The experiments were carried out on similar lines with increasing amounts of bentonite and in the presence of carbonates of barium and strontium in addition to magnesium and calcium carbonates.

The following mixtures were used for the present series of experiments :—

1. 1 g Bentonite + 80 ml Distilled water
2. 1.5 g „ + „ „ „
3. 2 g „ + „ „ „
4. 1.5 g (also 2 g) Bentonite + 80 ml Distilled water + 0.01 g $MgCO_3$.
5. „ „ „ + „ „ + 0.05 g „
6. „ „ „ + „ „ + 0.10 g „
7. „ „ „ + „ „ + 0.01 g $CaCO_3$.
8. „ „ „ + „ „ + 0.05 g „
9. „ „ „ + „ „ + 0.10 g „
10. 1.0 g (also 1.5 and 2.0 g) Bentonite 80 ml Distilled water + 0.01 g $SrCO_3$.
11. „ „ „ „ „ + 0.05 g „
12. „ „ „ „ „ + 0.10 g „
13. „ „ „ „ „ + 0.01 g $BaCO_3$
14. „ „ „ „ „ + 0.05 g „
15. „ „ „ „ „ + 0.10 g „
16. 80 ml. of Omeliansky's medium + 0.7 g $MgCO_3$.

RESULTS AND DISCUSSION

In our previous communication (1) we reported that the nitrosification in bentonite medium is favoured in the presence of optimum amounts of magnesium and calcium carbonates. Magnesium carbonate was found to be more suitable than calcium carbonate.

TABLE I
Nitrosification in Omeliansky's Medium

Concentration of Nitrite (mg./litre)						
Time in Hours						
48	96	144	192	240	288	336
0.425	1.555	8.8762	28.175	58.568	90.885	263.42

TABLE II
Nitrosification in Bentonite Medium.

Concentration of Nitrite (mg./litre)							
Nature of Medium	Time in Hours						
	48	96	144	192	240	288	336
1. 1.00 g.	0.1327	1.0222	3.2584	13.225	26.925	49.905	66.072
2. 1.50 g.	0.1327	1.1674	7.8396	16.675	42.139	79.140	111.695
3. 1.00 g.	0.1327	1.555	10.5540	28.175	52.825	83.211	136.325

TABLE III
(a) Effect of Calcium Carbonate on Nitrosification in Bentonite Medium.

Concentration of Nitrite (mg./litre)							
Nature of Medium	Time in Hours						
	48	96	144	192	240	288	336
1. 1.5 g. Bentonite alone.	0.1327	1.1674	7.8396	16.675	42.139	79.140	111.695
2. " + 0.01 g. CaCO ₃	0.1327	1.1674	7.8396	18.591	46.125	79.425	127.205
3. " + 0.05 g. CaCO ₃	0.1327	1.3416	8.0500	18.591	49.258	85.675	154.88
4. " + 0.100 g. CaCO ₃	0.1327	1.7250	9.2821	24.067	49.258	93.525	212.425

(b) Effect of Calcium Carbonate on Nitrosification in Bentonite Medium.

Nature of Medium	Concentration of Nitrite (mg./litre)						
	Time in Hours						
	48	96	144	192	240	288	336
1. 2.00 g. Bentonite alone.	0.1327	1.5550	10.554	28.175	52.825	83.211	136.925
2. „ + 0.01 g. CaCO ₃	0.1327	1.5550	10.554	28.175	56.925	85.675	143.175
3. „ + 0.05 g. CaCO ₃	0.1327	1.5550	10.554	28.175	61.716	102.925	190.585
4. „ + 0.10 g. CaCO ₃	0.1327	1.9250	13.225	33.925	61.716	108.425	229.425

As we observed (vide Table 2) that the extent of nitrosification could be increased provided the amount of bentonite used was also increased, we have studied the process with increasing amounts of bentonite and in the presence of magnesium, calcium, strontium and barium carbonates.

TABLE IV

(a) Effect of Magnesium Carbonate on Nitrosification in Bentonite Medium

Nature of Medium	Concentration of Nitrite (mg./litre)						
	Time in Hours						
	48	96	144	192	240	288	336
1. 1.5 g. Bentonite alone.	0.1327	1.1674	7.8396	16.675	42.139	79.140	111.695
2. „ + 0.01 g. MgCO ₃	0.1327	1.4790	9.5030	18.592	42.258	80.902	128.495
3. „ + 0.01 g. MgCO ₃	0.1327	1.6365	10.563	38.957	64.425	104.155	154.88
4. „ + 0.01 g. MgCO ₃	0.4250	3.8520	26.015	47.846	108.346	146.085	212.425

(b) Effect of Magnesium Carbonate on Nitrosification in Bentonite Medium

		Concentration of Nitrite (mg./litre)						
Nature of Medium		Time in Hours						
		48	96	144	192	240	288	336
1.	2.0 g. Bentonite alone.	0.1327	1.5550	10.554	28.175	52.825	83.211	136.325
2.	" + 0.01 g. MgCO ₃	0.2150	1.5550	9.275	28.175	59.425	93.917	146.855
3.	" + 0.05 g. MgCO ₃	0.2150	2.1630	13.195	41.692	74.221	108.345	163.725
4.	" + 0.10 g. MgCO ₃	0.4250	2.6190	16.653	56.925	114.425	163.725	249.425

TABLE V

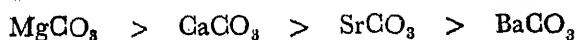
(a) Effect of Strontium Carbonate on Nitrosification in Bentonite Medium

Concentration of Nitrite (mg./litre)							
Nature of Medium	Time in Hours						
	48	96	144	192	240	288	336
1. 1.0 g. Bentonite alone.	0.1327	1.02220	3.2584	13.225	26.925	49.905	66.072
2. " + 0.01 g. $SrCO_3$	0.1327	1.11618	3.2584	13.225	31.369	50.5370	66.199
3. " + 0.01 g. $SrCO_3$	0.1327	1.2793	3.6416	13.225	46.125	58.568	88.225
4. " + 0.10 g. $SrCO_3$	0.425	1.2798	6.3250	16.675	48.079	62.152	100.552

(b) Effect of Strontium Carbonate on Nitrosification in Bentonite Medium

Concentration of Nitrite (mg./litre)							
Nature of Medium	Time in Hours						
	48	96	144	192	240	282	366
1. 1.5 g. Bentonite alone.	0.1327	1.1674	7.83960	16.675	42.139	79.140	111.695
2. " + 0.01 g. SrCO ₃	0.1327	1.555	8.504	19.725	47.650	79.425	136.329
3. " + 0.05 g. SrCO ₃	0.425	2.1630	16.675	41.5917	78.109	104.155	159.425
4. " + 0.10 g. SrCO ₃	0.425	2.1630	13.225	134.564	79.109	16.725	184.905

In the foregoing tables it may be seen that the effectiveness of the carbonates in stimulating the process in bentonite medium lies in the order.



(c) Effect of Strontium Carbonate on Nitrosification in Bentonite Medium.

Nature of Medium	Concentration of Nitrite (mg./litre)						
	Time in Hours						
	48	96	144	192	240	288	336
1. 2.0 g. Bentonite alone.	0.1327	1.5550	10.554	28.175	52.825	83.211	136.325
2. „ + 0.01 g. SrCO ₃	0.1327	1.5550	10.925	33.957	59.425	85.675	146.855
3. „ + 0.05 g. SrCO ₃	0.1327	2.8073	13.800	39.725	64.425	93.525	191.092
4. „ + 0.10 g. SrCO ₃	0.1327	1.825	9.008	14.425	48.079	73.425	129.175

TABLE VI

(a) Effect of Barium Carbonate on Nitrosification in Bentonite Medium

Nature of Medium	Concentration of Nitrite (mg./litre)						
	Time in Hours						
	48	96	144	192	240	288	336
1. 1.0 g. Bentonite alone.	0.1327	1.02220	3.2584	13.2230	26.925	49.095	66.072
2. „ + 0.01 g. BaCO ₃	0.1327	2.6194	10.5630	24.7515	49.258	66.199	94.0170
3. „ + 0.05 g. BaCO ₃	0.1327	0.7622	1.6365	4.5362	9.879	25.963	46.125
4. „ + 0.10 g. BaCO ₃	0.1327	0.7622	1.1490	4.255	5.175	5.6980	8.292

(b) Effect of Barium Carbonate on Nitrosification in Bentonite Medium

Nature of Medium	Concentration of Nitrite (mg./litre)						
	Time in Hours						
	48	96	144	192	240	288	336
1. 1.5 g. Bentonite alone.	0.1327	1.16740	7.83960	16.675	42.139	79.140	111.695
2. „ + 0.01 g. BaCO ₃	0.4250	2.1630	19.725	48.079	82.255	91.095	126.925
3. „ + 0.05 g. BaCO ₃	0.1327	1.068	8.505	19.725	43.366	68.425	119.225
4. „ + 0.10 g. BaCO ₃	0.1327	0.7622	1.068	1.425	1.7250	2.6194	8.8340

(c) Effect of Barium Carbonate on Nitrosification in Bentonite Medium

Nature of Medium	Concentration of Nitrite (mg./litre)						
	Time in Hours						
	48	96	144	192	240	288	336
1. 2.0 g. Bentonite alone.	0.1327	1.5550	10.554	28.175	52.825	83.211	136.325
2. „ + 0.01 g. BaCO ₃	0.4250	1.5550	9.2821	25.763	58.568	93.5159	139.665
3. „ + 0.05 g. BaCO ₃	0.1327	1.411	5.667	10.925	25.763	60.307	88.288
4. „ + 0.10 g. BaCO ₃	0.1327	0.575	1.068	1.3420	1.925	4.355	5.175

With 1.5 g. and 2.0 g. of bentonite, both magnesium carbonate and calcium carbonate appear to be equally effective. Strontium carbonate is not as good and barium carbonate is definitely unfavourable.

TABLE VII

Effect of the Ratio between the Carbonates and Bentonite on Nitrosification in Bentonite Medium

Nature of Carbonates	1.0 g. Bentonite			1.5 g. Bentonite			2.0 g. Bentonite		
	Ratio		Concentration of nitrite mg./litre	Ratio		Concentration of nitrite mg./litre	Ratio		Concentration of nitrite mg./litre
	Carbonate	Bentonite		Carbonate	Bentonite		Carbonate	Bentonite	
MgCO ₃ ...	1:100		96.2471	1:150		128.485	1:200		146.855
	1:20		240.5078	1:130		154.88	1:40		163.725
	10		68.0955	1:15		212.425	1:20		249.425
CaCO ₃ ...	1:100		80.1999	1:150		127.205	1:200		143.175
	1:20		199.3961	1:30		154.88	1:40		190.585
	1:10		105.5843	1:15		212.425	1:20		229.425
SrCO ₃ ...	1:100		66.199	1:150		136.329	1:200		146.855
	1:20		88.225	1:30		159.425	1:40		191.092
	1:10		100.552	1:15		184.905	1:20		129.175
BaCO ₃ ...	1:100		94.017	1:150		126.925	1:200		139.665
	1:20		46.125	1:30		119.225	1:40		88.288
	1:10		8.292	1:15		8.834	1:20		5.175

From the Table 7, it appears that maximum nitrosification can occur if the ratio between the amounts of the first two effective carbonates and bentonite is maintained near about 1:20. To obtain as good results as in Omeliansky's medium, it would be better if the bentonite medium is made to consist of 0.1 g. either of magnesium or calcium carbonates and 2.0 g. of bentonite. For strontium carbonate, best ratio appears to be 1:15 and 1:40. In the case of barium carbonate, there is definite indication, that the process of nitrosification is only favoured when for a definite concentration of barium carbonate the amount of bentonite to be used is very high.

ACKNOWLEDGMENT

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REFERENCE

1. Tandon, S. P., De, S. K. and Rastogi, R. C., Bentonite as a growth medium for nitrifying bacteria (*Nitrosomonas* Part I. *N. Jb. Miner. Mh.* 2, 42 (1962).

STUDIES OF THE THERMODYNAMIC FUNCTIONS OF IONISATION OF VANILLIC ACID

By

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ABSTRACT

pK values for the ionisation of the Carboxyl group of vanillic acid have been determined pH metrically at different temperatures in the range 25°C to 60°C. The variation of pK with temperature has been found to obey an equation of the type of Harned and Robinson. From the parameters of this equation, the thermodynamic functions of ionisation such as change in free energy, entropy, heat content and heat capacity have been computed. The influence of the substituents on the ionization of the parent acid has been discussed and the applicability of the free energy additivity relationship has been examined. The consideration of the entropy of ionization indicates that no significant energy differences are involved in the molecule-solvent and the anion-solvent inter-actions.

The influence of substituents on the strength of acids has been for long interpreted in terms of the polar effects of the substituent groups. Certain investigations in case of aliphatic acid¹⁻³ and our investigations on substituted benzoic acids⁴⁻⁶ have, however, shown that sometimes factors such as hydrogen bonding, solvation, etc., significantly modify the polar effects of the substituents. Thus, for example, in spite of the greater electron withdrawing power of the hydroxyl than that of the methoxyl group, gallic acid has been found to be weaker than the corresponding 3, 4, 5-trimethoxy benzoic acid⁴⁻⁵. Since solvent effects involve a significant change in the entropy of ionisation we considered it of value to extend our pH metric studies on the determination of thermodynamic functions of ionisation, to various hydroxy and/or methoxy benzoic acids; the present communication reports the results of our investigation on vanillic acid.

EXPERIMENTAL

Vanillic acid was obtained by the oxidation of vanillin by silver oxide⁷; repeated recrystallisation of the product from water, gave a sample with M. P. 210°C. Sodium hydroxide used was guaranteed reagent (Merck). Solution of this reagent used for pH metric titration of vanillic acid was standardised by titrating against oxalic acid.

All the pH metric measurements were made with a Beckman pH meter (model G) having an accuracy of 0.01 pH unit; temperature corrections were made above 40°C using the correction factors given in the instructions for the instrument. The titrations were carried out in an oil thermostat. The temperature of the system was controlled with a precision of $\pm 0.02^\circ\text{C}$, details about which have been described earlier⁸. Purified nitrogen with oxygen content <0.5% was bubbled through the solutions before and during the titrations.

RESULTS AND DISCUSSION

Fig. 1 gives the pH metric titration curves of vanillic acid at different temperatures in the range 25-60°C. These data indicate that unlike other acids having non-ionisable substituents, the range of pH change near neutralization point was not considerable for vanillic acid. This is because of the fact that the acid has, besides the carboxyl group, another ionisable group, viz, the hydroxyl. Since we were primarily interested in the ionisation of carboxyl group, no attempt was made to titrate the acid beyond the neutralization of the carboxyl group. From these data, the classical ionisation constants (k) of the acid at different temperatures were obtained in the usual manner⁹.

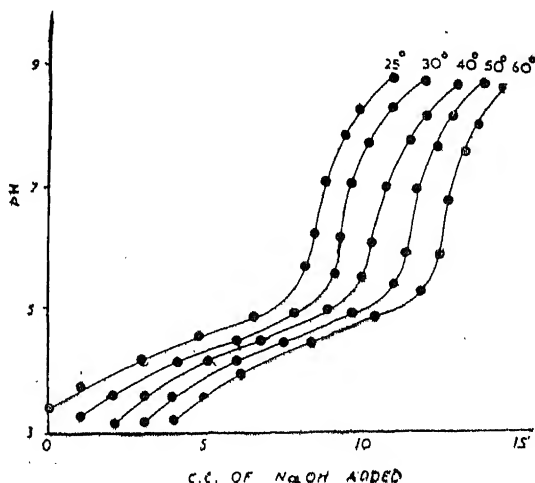


Fig. 1. pH metric Titration Curves of Vanillic Acid

The classical (law of mass action) ionisation constants are known to vary with the ionic strength of the system. In order to get the values of thermodynamic ionisation constant the use of modified Debye-Huckel equations¹⁰ gave the relationship:

$$pK = pK + \frac{2A_1 Z_1^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad (1)$$

where the symbols have their usual meanings. The values of the constant A_1 employed in these calculations were due to Bates and coworkers¹¹. Further, the ionic strength of the system at different stages of titrations was calculated in the usual manner and it was assumed that the activity coefficient of undissociated molecule is unity. The values of pK obtained at different temperatures are given in column 3 of Table 1.

TABLE I
Ionisation Constants of Vanillic Acid at Different Temperatures

Temperature °A	pK	pK
298	4.45	4.47
303	4.41	4.43
313	4.36	4.39
323	4.42	4.44
333	4.46	4.48

It is seen from the data in table I that like various other acids pK values of vanillic acid are markedly influenced by temperature. Fig. 2 gives the variation

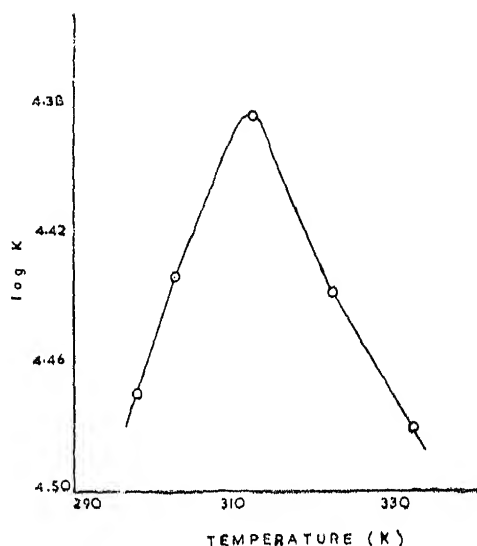


Fig. 2. Variation of $\log K$ with temperature

of $\log K$ with temperature and it is of interest to note that the value of K attains a maximum. This behaviour is exhibited by various other acids involving ionisation of the carboxyl group. The variation of pK with temperature was described by an equation of the type given by Harned and Robinson¹²

$$-\ln K = \frac{1.956 \times 10^4}{T} - 110.85 + 0.219T \quad (2)$$

The constants in the right handside of the above equation were evaluated by the solution of simultaneous equations set up with two variables viz. pK and T. The applicability of the above equation was examined by calculating the values of pK at various temperatures using the above equation. Excellent agreement was observed between the calculated and experimental values at a temperature close to T_{\max} , the temperature where the value of K is maximum. There were noticeable certain deviations between these calculated and observed values especially at elevated temperatures. Similar observations regarding close agreement especially at T_{\max} have been observed earlier¹³ and in fact it was suggested by Harned and Embree¹⁴ that comparison of acid strength should be made at T_{\max} rather than at an arbitrary temperature such as 293°A. This approach has however not been found to have any advantage^{1,15} and moreover the knowledge of acid strength at 298°A of unsubstituted and other substitutes benzoic acids helps better understanding of the substituent effect. Thermodynamic functions associated with ionisation of carboxyl group of vanillic acid were calculated at 298°A using the constants of Eq. (2) and employing the well known relationships¹². These values are given in table 2

TABLE 2
Thermodynamic Functions of Ionisation of Vanillic Acid at 25°C

ΔF	5.927	K. Cals./mole.
ΔH	145.1	K. Cals./mole.
ΔS	-19.50	Cals/deg./mole.
ΔC_p	-130.3	Cals/deg./mole.

The difference between the acid strength of vanillic acid and benzoic acid can be explained in terms of the influence of the substituents (methoxyl in meta and hydroxyl in para) on the pK of benzoic acid. It is known that meta substitution of methoxyl group in benzoic acid (pK 4.174) caused the lowering of pK unsubstituted acid (m-methoxy benzoic acid pK 4.055) by 0.12 unit due to -I effect of the methoxyl group; while para substitution of hydroxyl group in benzoic acid resulted in increase of pK of *p*-hydroxy benzoic acid (pK 4.537) by 0.363 unit due to electron attracting nature of the carboxylic group and electron repelling nature of the hydroxyl groups^{16,17}. The application of the additivity principle^{19,20} thus gives a values of 4.421 (at 25°C). Similarly the application of linear free energy relationship gave a theoretical value of 6.385 K. cal. for ΔF which agrees closely with the experimentally determined result.

It has been shown by Pitzer²¹ that the changes in entropy of ionisation are paralleled by the differences in the energies of interaction between the acid and the solvent, and the anion and the solvent. Since the difference in ΔS for vanillic acid and benzoic acid²³ is not significant, it follows that the energy considerations involved in the interaction with the solvent are not appreciable. This deduction is in accord with the fact that there is little electro-striction of water molecule by the COO^- group; this is because of its large size and the smearing of charge over the two oxygen atoms due to resonance²².

REFERENCES

1. E. J. King, *J. Am. Chem. Soc.*, **82**, 3575 (1960).
2. L. P. Farnandez and L. G. Helper, *J. Am. Chem. Soc.*, **81**, 1783, (1959).
3. F. S. Feates and D. S. G. Ives, *J. Am. Chem. Soc.*, **78**, 2798 (1956).
4. N. A. Ramaiah and R. K. Chaturvedi, *Proc. Ind. Acad. Sci.*, **51**, 177 (1960).
5. R. K. Chaturvedi and S. S. Katiyar, *J. Sci & Ind. Res.*, **21B**, 47 (1962).
6. R. K. Chaturvedi and S. S. Katiyar, *Bull. Chem. Soc. Japan*, **35**, 1416 (1962).
7. I. A. Pearl, *J. Am. Chem. Soc.*, **68**, 1100 (1946).
8. N. A. Ramaiah and R. K. Chaturvedi, *Z. phys. Chem.* **214**, 184 (1960).
9. H. T. S. Britton, "Hydrogen Ions", Chapman & Hall, London 4th Edition, 1955, p. 217.
10. E. A. Guggenheim and F. Schindler, *J. Phys. Chem.*, **38**, 539 (1934).
11. G. G. Manov, R. G. Bates, W. H. Hamer and S. E. Acree, *J. Am. Chem. Soc.*, **65**, 1765 (1943).
12. H. S. Harned and R. A. Robinson, *Trans. Far. Soc.*, **36**, 973 (1940).
13. R. G. Bates and G. D. Pinching, *J. Am. Chem. Soc.*, **71**, 1274 (1949).
14. H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1050 (1934).
15. E. J. King and G. W. King, *J. Am. Chem. Soc.*, **78**, 1098 (1956).
16. L. A. Wiles, *Chem. Revs.* **56**, 329 (1956).
17. J. F. J. Dippp, *Chem. Revs.*, **25**, 151 (1939).
18. D. H. Mathews and T. R. Welch, *J. Appl. Chem.*, **8**, 711 (1958).
19. J. Shorter and F. J. Stubbs, *J. Chem. Soc.*, 1180 (1949).
20. H. C. Brown, D. H. McDaniel and O. Hafliger in "Determination of Organic Structures by Physical Methods," Ed. E. A. Braude and F. C. Nachod, Acad. Press Inc., New York, 1955 p. 587.
21. K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365, (1937).
22. T. W. Zawidzki, H. M. Papee and K. J. Laidler, *Trans. Far. Soc.*, **55**, 1744, (1959).

ON STABILITY OF NON-LINEAR SYSTEMS OF DIFFERENTIAL EQUATIONS

By

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ABSTRACT

The author discusses the stability of the trivial solution of the non-linear system of differential equations,

$$\frac{dx}{dt} = A(t)x + f(t, x) \quad (B)$$

in the sense of Liapunov. The author employs a lemma, which is an extension of another lemma established by the author in an earlier communication, to (B). This essentially depends on the notion of Liapunov's scalar function and the maximal solution of an auxiliary equation. In theorem I, the author takes the simpler case when the matrix A (square) is a constant. In Theorem II, the result of the Theorem I is extended to the case when the matrix $A(t)$ (square) is a continuous function of t for $t \geq 0$.

1. The purpose of this note is to discuss the stability of trivial solution of the non-linear systems of differential equations in the sense of Liapunov [3]. The main result of this note is essentially analogous to [2]. However, the author has employed altogether different technic and less restrictive conditions in obtaining the same. In § 2 we shall establish a lemma, which will play an important role in our discussion and which is only an extension of the lemma established by the author [4] for (2.1).

2. We consider the system of differential equations

$$\frac{dx}{dt} = A(t)x + f(t, x) \quad (2.1)$$

where x denotes a n -dimensional vector and $f(t, x)$ is a given vector field which is defined in the product space $\Delta = I \times R^n$ and continuous there, where I is the interval $0 \leq t < \infty$ and R^n is Euclidean space of n dimensions. $A(t)$ is $n \times n$ matrix. Let $V(t, x(t)) \geq 0$ be a scalar function also defined on Δ . We assume that V satisfies a Lipschitz condition in x locally. We define

$$V^*(t, x) = \lim_{h \rightarrow 0+} \sup \frac{1}{h} \left[V(t+h, x + h A(t)x) - V(t, x) \right] \quad (2.2)$$

Lemma :

Let $\omega(t, r)$ be measurable in t for fixed r and continuous in r for fixed t . Suppose

$$V^*(t, x) \leq \omega(t, V(t, x)) - \alpha V(t, x) \quad (2.3)$$

where $\alpha > 0$ is a suitably chosen number.

Further, let

$$|f(t, x)| \leq V(t, x) \quad (2.4)$$

where $|x|$ indicates the Euclidean norm of x .

Let $r(t)$ be the maximal solution of

$$r' = \omega(t, r) \quad (2.5)$$

with $r(t_0) \leq r_0, r_0 > 0$. Then if $x(t)$ is any solution of

(2.1) such that $V(t_0, x(t_0)) \leq r_0$, we have

$$V(t, x(t)) \leq r(t) \quad \text{for } t \geq t_0. \quad (2.6)$$

Proof: As V satisfies a Lipschitz condition in x , we have

$$\begin{aligned} V(t+h, x+hA(t)x+hf(t,x)) - V(t,x) \\ = V(t+h, x+hA(t)x+hf(t,x)) - V(t+h, x+hA(t)x) \\ + V(t+h, x+hA(t)x) - V(t,x) \\ \leq K|f(t,x)| + V(t+h, x+hA(t)x) - V(t,x) \end{aligned} \quad (2.7)$$

where K is some constant. It then follows using (2.2), (2.3), (2.4) and (2.7)

$$\begin{aligned} \lim_{h \rightarrow 0} \sup \frac{1}{h} [V(t+h, x+hA(t)x+hf(t,x)) - V(t,x)] \\ \leq \omega(t, V(t,x)). \end{aligned} \quad (2.8)$$

Let $x(t)$ be any solution of (2.1).

Define $V(t, x(t)) = m(t)$. Then we have for sufficiently small $\epsilon > 0$

$$\frac{x(t+h) - x(t)}{h} = A(t)x + f(t,x) + \epsilon. \quad (2.9)$$

Again

$$\begin{aligned} m(t+h) - m(t) &= V(t+h, x+hA(t)x+hf(t,x)+h\epsilon) - V(t,x) \\ &\leq K|\epsilon h| + V(t+h, x+hA(t)x+hf(t,x)) - V(t,x). \end{aligned}$$

Therefore we get

$$\lim_{h \rightarrow 0} \sup \frac{1}{h} \left[m(t+h) - m(t) \right] \leq \omega(t, m(t)). \quad (2.10)$$

Now the rest of the proof of the lemma is essentially the same as in [4], hence omitted.

3. Let us consider the equation

$$\frac{dx}{dt} = Ax + f(t, x) \quad (3.1)$$

where A is a constant matrix (square).

consider simultaneously the vector equation

$$\frac{dy}{dt} = Ay \text{ with } y(0) = z(0) = c \quad (3.2)$$

where c is a constant vector and the matrix-matrix equation

$$\frac{dY}{dt} = AY, \text{ with } Y(0) = E \quad (3.3)$$

where E is the identity matrix and $|Y| \leq c_1$ where c_1 is a constant.

Theorem 1. If

(i) $f(t, x)$ satisfies the conditions of the lemma in § 2,

(ii) all the solutions of (3.2) are bounded for $t \geq 0$, (e.g. the real parts of the characteristic roots of A are negative or zero and in the latter case they are simple),

(iii) $\int_0^\infty \frac{dt}{r(t)}$ is divergent, where $r(t)$ is the maximal solution of the equation

$r' = \omega(t, r)$ as in the lemma, then the trivial solution $x = 0$ of (3.1) is stable

Proof: Every solution of (3.1) satisfies the non-linear integral equation [1]

$$x(t) = y(t) + \int_0^t Y(t-\tau) f(\tau, x(\tau)) d\tau.$$

Therefore we have

$$|x(t)| \leq c_1 |c| + c_1 \int_0^t V(\tau, x(\tau)) d\tau.$$

Let us put

$$U(t) = c_1 |c| + c_1 \int_0^t V(\tau, x(\tau)) d\tau, \text{ then}$$

$$U'(t) = c_1 V(t, x(t)) \quad (3.4)$$

If we have $M(z) = \int_{z_1}^z [r(s)]^{-1} ds$, then from (3.4) and (2.6)

$$\frac{d}{dt} M(U(t)) \leq c_1 \quad (3.5)$$

Integrating between 0 and t , we have

$$M(U(t)) \leq M(U(0)) + c_1 t \quad \text{or}$$

$$U(t) \leq M^{-1}[M(U(0)) + c_1 t], \text{ where } M^{-1}(z) \text{ is the inverse of } M(z).$$

Therefore we have

$$|x(t)| \leq M^{-1}[M(c_1 |c|) + c_1 t] \quad (3.6)$$

By the condition (iii) of the theorem, the right hand side of (3.6) is less than an arbitrarily small positive number for $t \geq 0$ which is equivalent to the stability of the trivial solution of (3.1) in the sense of Liapunov.

4. Consider now the equation

$$\frac{dx}{dt} = A(t)x + f(t, x) \quad (4.1)$$

where matrix $A(t)$ (square) is also a function of t .

We consider simultaneously the equation

$$\frac{dy}{dx} = A(t)y \quad (4.2)$$

with $y(0) = x(0) = C$, where C is a constant vector, and

$$\frac{dY}{dt} = A(t) Y \quad (4.3)$$

with $Y(0) = E$.

Theorem 2. If

(i) $A(t)$ is continuous for $t \geq 0$ and $\lim_{t \rightarrow \infty} \int_0^t \text{tr}(A) dt > -\infty$ or in particular

$\text{tr}(A) \equiv 0$, ($\text{tr}(A)$ means the trace of $A(t)$),

(ii) every solution of (4.2) is bounded,

(iii) $\int_0^\infty \frac{dt}{r(t)}$ is divergent, then the trivial solution $x = 0$ of (4.1) is stable.

Proof: Every solution of (4.1) satisfies the non-linear integral equation

$$x(t) = y(t) + \int_0^t Y(t) Y^{-1}(\tau) f(\tau, x(\tau)) d\tau$$

where $Y^{-1}(t)$ is the inverse of $Y(t)$. Now

$$\det Y(t) = e^{\int_0^t \text{tr}(A) dt}$$

Therefore, on account of the condition (i)

$|Y^{-1}(t)|$ is bounded.

Let $c_1 = \sup |Y|$, $c_2 = \sup |Y^{-1}|$, then

$|y| \leq c_1 |C|$ and writing for c_1, c_2, c_3 , we have

$$|x(t)| \leq c_1 |C| + c_2 \int_0^t V(\tau, x(\tau)) d\tau.$$

Therefore as in theorem 1, we get

$$|x(t)| \leq M^{-1} [M(c_1 |C|) + c_3 t].$$

To establish the stability of trivial solution of (4.1), we argue as in theorem 1.

REFERENCES

1. Bellman, R. Stability Theory of differential equations. McGraw Hill, 1953, pp. 80.
2. Bihari, I, Researches of the boundedness and stability of solutions of non-linear differential equations. *Acta Mathematica, Acad. Sc. Hungary*, Vol. VIII, 1957, pp. 261—278.
3. Birkhoff, G. D. Dynamical systems. Amer. Math. Soc. Colloq. Pub. 1927, pp. 124.
4. Jagdish Chandra. "On the asymptotic Behaviour of solutions of non-linear differential equations. *Proc. Nat. Acad. Sc., India, Sec. A*, Vol. XXXII, Part II, 1962, pp. 148—151,

KINETICS OF OXIDATION OF PROPIONALDEHYDE BY PERSULPHATE ION IN AQUEOUS SOLUTION

By

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ABSTRACT

1. The molar ratio of propionaldehyde and potassium persulphate reacting has been found to be 1:1.
2. The overall order of the silver-catalysed reaction is one. The order with respect to $S_2O_8^{2-}$ is one while the order with respect to propionaldehyde is zero.
3. At higher concentrations of propionaldehyde, the reaction is attended with an induction period, the extent of induction increasing with an increase in propionaldehyde concentration, which is likely to be due to the dissolved oxygen or due to propane impurity in traces.
4. The salt effect in presence of K_2SO_4 is negative and of the primary exponential type.
5. The specific ionic effect is in the order $K^+ > Na^+ > Mg^{++} > NH_4^+$. In presence of NH_4^+ the rate increases instead of decreasing as is the case with other ions.
6. The rate for the silver ion catalysed reaction has been found to be linearly related to $AgNO_3$ concentration.
7. The temperature coefficient and the energy of activation have been found to be 1.86 and 11.863 Cals per gram mol. respectively. From these values the frequency factor and entropy of activation have been calculated.
8. There is no perceptible effect of H^+ ions on this reaction.

INTRODUCTION

During the course of the systematic study of the kinetics of oxidation of ketones¹ and aldehydes (formaldehyde² and acetaldehyde³), it was observed by us that whereas the oxidation of ketones by persulphate ion proceeded in a smooth manner, the results in the case of oxidation of aldehydes (especially formaldehyde) by persulphate ion were fairly erratic. Further it was observed that the rate of oxidation of acetaldehyde was greater than that of formaldehyde. This erratic behaviour and abnormal nature of the oxidation of lower aldehydes led us to undertake the present study of the kinetics of oxidation of propionaldehyde by persulphate ion.

EXPERIMENTAL

Recrystallised potassium persulphate, G. R., E. Merck and propionaldehyde of B.D.H. quality were used. The standard solution of potassium persulphate was made by direct weighing of the salt and was standardised by iodometric method of Szabo, Csanyi and Galiba⁴ as modified by the authors in the kinetic study of oxidation of aldehydes (*loc. cit.*). The standard solution of propionaldehyde was prepared by dissolving the calculated volume in water and estimating it by hydroxylamine hydrochloride pyridine procedure for aldehydes and ketones (*vide* Vogel — Quantitative Organic Analysis). The other salts viz. $AgNO_3$, K_2SO_4 , Na_2SO_4 , $MgSO_4$ and $(NH_4)_2SO_4$ were all of A.R., B.D.H. quality. The experimental technique followed was the same as followed in our previous studies (*loc. cit.*) and redistilled water from a Pyrex distilling still was always used for making up the solutions and as the medium for carrying out the reaction.

Determination of molar ratio of reactants.—In order to determine the molar ratio of $K_2S_2O_8$ and C_2H_5CHO in the reaction, two sets of experiments were conducted, employing in each case an excess of $K_2S_2O_8$. The reaction mixture was kept at a temperature of nearly $35^\circ C$. for 100 hours in each case and the amount of $K_2S_2O_8$ remaining at various intervals of time was determined by pipetting out 5 c.c. of the reaction mixture in each case. In both the sets of experiments, $K_2S_2O_8$ in presence of $AgNO_3$ alone was also kept in the same bath for the same interval of time and the amount of its decomposition was also determined. From these data, the amount of $K_2S_2O_8$ reacting with propionaldehyde in each set was calculated.

TABLE I

Time in hours	Set I		Set II	
	Expt. I $C_2H_5CHO =$ 0.01 M	Expt. II $K_2S_2O_8 =$ 0.04 M	Expt. I $C_2H_5CHO =$ 0.01 M	Expt. II $K_2S_2O_8 =$ 0.03 M
	$K_2S_2O_8 =$ 0.04 M	$AgNO_3 =$	$K_2S_2O_8 =$ 0.03 M	$AgNO_3 =$
	$AgNO_3 =$ 0.0002 M	0.0002 M	$AgNO_3 =$ 0.0002 M	0.0002 M
	Volume of 0.02 in ml., equiv. concentration.	N $Na_2S_2O_3$ to $K_2S_2O_8$	Volume of 0.02 in ml., equiv. concentration.	N $Na_2S_2O_3$ to $K_2S_2O_8$
0	20.00	20.00	15.00	15.00
27	9.25	14.88	5.80	10.95
50	7.15	12.90	4.20	9.15
100	3.60	8.90	1.50	6.40

From the above data it is seen that in Set I the amount of $K_2S_2O_8$ consumed in 100 hours in experiment I corresponds to 16.4 ml; while in experiment II to 11.1 ml. The difference of these values should correspond to the amount of $K_2S_2O_8$ consumed by propionaldehyde. This comes out to be 5.3 ml. which corresponds to 0.0106 M of $K_2S_2O_8$. Since the concentration of propionaldehyde taken is 0.01 M, it leads us to conclude that 1 mol. of $K_2S_2O_8$ reacts with 1 mol. of C_2H_5CHO . Similarly in the second set, the amounts of $K_2S_2O_8$ consumed in experi-

ment I and II are equivalent to 13.5 and 8.6 ml., the difference of which is 4.9 ml., which corresponds to 0.0098 M of $K_2S_2O_8$. This again shows that one molecule of $K_2S_2O_8$ reacts with one molecule of propionaldehyde.

The kinetic study of the reaction was then undertaken in the presence of $AgNO_3$ as catalyst, one such set of observations being recorded below :—

TABLE 2

$K_2S_2O_8 = 0.01 \text{ M}$; $CH_3CH_2CHO = 0.01 \text{ M}$; $AgNO_3 = 0.001 \text{ M}$;
Temperature 35°C .

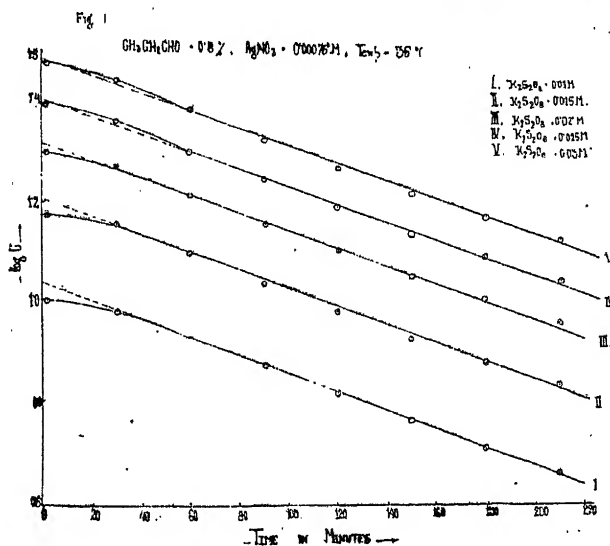
Time in minutes	Conc. of $K_2S_2O_8$ (In terms of 0.01 N $Na_2S_2O_8$ in ml.)	$k \times 10^3$ (Unimolecular)
2	19.90	—
15	18.84	4.2162
30	17.63	4.3620
45	16.50	4.3595
60	15.50	4.3121
90	13.60	4.3282
120	11.99	4.2949
150	10.46	4.3492
180	9.14	4.3731
Mean		4.3244

A fair constancy of the first order rate constant obtained at equimolecular concentration of the reactants shows that the over-all order of the reaction is one.

Effect of $K_2S_2O_8$ concentration :—In order to determine the dependence of the rate on the concentration of the reactants the reaction was first of all carried out at four different initial concentrations of $K_2S_2O_8$, keeping the concentration of propionaldehyde and $AgNO_3$ constant. The results of these experiments are tabulated below,

TABLE 3
 $\text{CH}_3\text{CH}_2\text{CHO} = 0.8\%$, $\text{AgNO}_3 = 0.0075 \text{ M}$; Temp. 35°C .
 (by weight)

Time in minutes	Expt. 1 $\text{K}_2\text{S}_2\text{O}_8 = 0.01 \text{ M}$		Expt. 2 $\text{K}_2\text{S}_2\text{O}_8 = 0.015 \text{ M}$		Expt. 3 $\text{K}_2\text{S}_2\text{O}_8 = 0.02 \text{ M}$		Expt. 4 $\text{K}_2\text{S}_2\text{O}_8 = 0.025 \text{ M}$		Expt. 5 $\text{K}_2\text{S}_2\text{O}_8 = 0.03 \text{ M}$	
	Vol. of 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ in ml., equiv. to $\text{K}_2\text{S}_2\text{O}_8$ conc.	$k \times 10^3$ (uni.)	Vol. of 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ in ml., equiv. to $\text{K}_2\text{S}_2\text{O}_8$ conc.	$k \times 10^3$ (uni.)	Vol. of 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$ in ml., equiv. to $\text{K}_2\text{S}_2\text{O}_8$ conc.	$k \times 10^3$ (uni.)	Vol. of 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$ in ml., equiv. to $\text{K}_2\text{S}_2\text{O}_8$ conc.	$k \times 10^3$ (uni.)	Vol. of 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$ in ml., equiv. to $\text{K}_2\text{S}_2\text{O}_8$ conc.	$k \times 10^3$ (uni.)
2	20.20	—	14.90	—	19.95	—	24.80	—	29.90	—
30	19.15	1.9164*	14.14	1.8753*	18.78	2.1928*	23.06	2.6073*	27.81	2.5579*
60	17.08	2.9025*	12.47	3.0733	16.31	3.5155	19.90	3.6218	24.11	3.7125
90	15.00	3.3838	10.29	3.5645	14.30	3.7867	17.50	3.9524	21.05	3.9795
120	13.20	3.6067	9.56	3.7609	12.65	3.8624	15.50	3.9853	18.66	3.9970
150	11.64	3.7252	8.51	3.7860	11.24	3.8779	13.76	3.9639	16.56	3.9929
180	10.30	3.7859	7.66	3.7390	10.25	3.7448	12.45	3.8737	15.00	3.8655
210	9.25	3.7567	6.94	3.6737	9.21	3.7121	11.19	3.8298	13.56	3.8033
Mean		3.6516		3.7048		3.7498		3.8711		3.8917



An examination of the above data shows that the reaction at high concentration of propionaldehyde is characterised by an induction period, the extent of the induction effect decreasing with an increase in $K_2S_2O_8$ concentration. Except for the initial stages the reaction is first order with respect to $K_2S_2O_8$. A linear curve is obtained when we plot $\log (S_2O_8)''$ against time. Further, the time for half decomposition of $K_2S_2O_8$ from these curves comes out to be 187, 187, 181, 179 and 181 minutes for 0.01 M, 0.015 M, 0.02 M, 0.025 M and 0.03 M $K_2S_2O_8$ concentrations respectively. This definitely shows that the reaction is first order with respect to $K_2S_2O_8$.

Effect of Propionaldehyde concentration :—

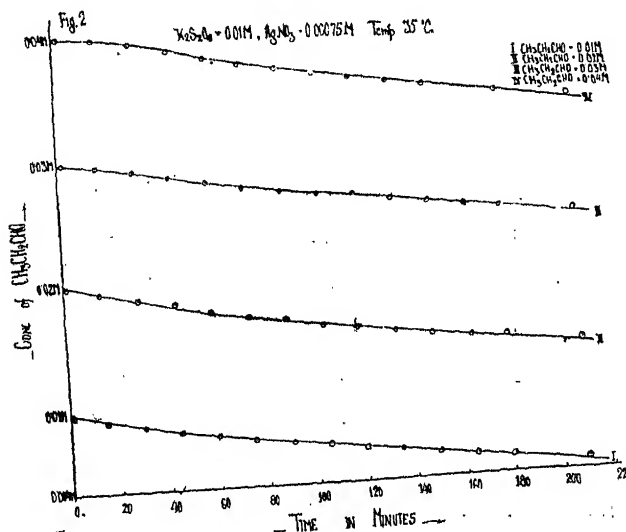
In order to study the effect of propionaldehyde concentration on the rate, the reaction was studied at four different initial concentrations of propionaldehyde, the results of which are tabulated below.

TABLE 4

$K_2S_2O_8 = 0.01 \text{ M}$; $AgNO_3 = 0.00075 \text{ M}$; Temperature $35^\circ C$.

Time in minutes	0.02 M CH_3CH_2CHO		0.03 M CH_3CH_2CHO		0.04 M CH_3CH_2CHO	
	Vol. of 0.01 N $Na_2S_2O_3$ in ml.	$k \times 10^3$ (uni)	Vol. of 0.01 N $Na_2S_2O_3$ in ml.	$k \times 10^3$ (uni)	Vol. of 0.01 N $Na_2S_2O_3$ in ml.	$k \times 10^3$ (uni)
2	20.15	—	19.90	—	19.95	—
15	19.28	3.2242	19.29	2.4270	19.59	1.4349
30	18.09	3.7670	18.08	3.4298	18.52	3.0219
45	17.04	3.7501	16.92	3.7758	17.26	3.4671
60	15.95	3.9865	15.94	3.6553	16.28	3.5101
75	15.14	3.8287	14.98	4.0313	15.29	3.6501
90	14.34	3.8403	14.12	4.0156	14.39	3.7188
105	13.50	3.8853	13.23	3.9642	13.55	3.7585
120	12.87	3.7994	12.76	3.6839	12.73	3.8520
135	12.28	3.7263	12.00	3.8042	12.16	3.7545
150	11.60	3.7143	11.35	3.7965	11.49	3.7314
180	10.47	3.6757	11.26	3.7260	10.31	3.7106
210	9.44	3.6339	9.26	3.6792	9.25	3.6969

The data corresponding to 0.01 M propionaldehyde are recorded in table 2. When the log of the titre values after conversion into propionaldehyde concentra-



tion are plotted against time, linear curves are obtained, indicating that the reaction is zero order with respect to propionaldehyde concentration. From these curves the time for $\frac{1}{4}$ th decomposition is 76 and 180 minutes in case of 0.01 M and 0.02 M concentration, showing that the order of the reaction with respect to propionaldehyde is less than 1. The time for $\frac{1}{8}$ th decomposition comes out to be 32, 71, 127 and 177 minutes for 0.01, 0.02, 0.03 and 0.04 M propionaldehyde concentrations respectively. On substitution in the formula $n = 1 + \log(t_1/t_2)/\log(a_2/a_1)$, the value of n comes out to be -0.15, -0.25, -0.43, -0.31 and -0.15 showing that the order with respect to propionaldehyde is zero. However, it is seen that the reaction is attended with an induction period at higher concentration of propionaldehyde, which may be attributed to the presence of some trace of impurity present in propionaldehyde, probably propane.

Effect of temperature:—In order to determine the temperature coefficient and energy of activation the reaction was carried out at different temperatures from 25° to 45°C. The temperature coefficient for the Ag^+ catalysed reaction between this temperature range is 1.86 and the energy of activation comes out to be 11863.3 cal. The frequency factor and the entropy of activation are 1.987×10^4 litre mols. sec^{-1} and -38.79 E.U. respectively. The Arrhenius equation is applicable to this reaction within this temperature range.

Salt effect:—To determine the nature of the salt effect, K_2SO_4 was used as the neutral salt. The results in presence of different concentrations of K_2SO_4 are summarised below:—

TABLE 5

$\text{CH}_3\text{CH}_2\text{CHO} = 0.01 \text{ M}$; $\text{K}_2\text{S}_2\text{O}_8 = 0.01 \text{ M}$; $\text{AgNO}_3 = 0.001 \text{ M}$;
Temp. 35°C .

Conc. of K_2SO_4	μ	$(\mu)^{\frac{1}{2}}$	$k \times 10^3$	Log k
0.00 M	0.03	0.173	4.3244	-2.3641
0.01 M	0.06	0.244	3.7741	-2.4232
0.015 M	0.075	0.273	3.5500	-2.4498
0.02 M	0.09	0.300	3.2553	-2.4875
0.03 M	0.12	0.346	3.0637	-2.5139
0.04 M	0.15	0.387	2.8899	-2.5392

It is seen that with an increase in salt concentration, the rate decreases. When the value of $(\mu)^{\frac{1}{2}}$ is plotted against log k , the curve is closely linear, showing thereby that the negative salt effect is of the primary exponential type. This suggests that the rate determining process is between two oppositely charged ions.

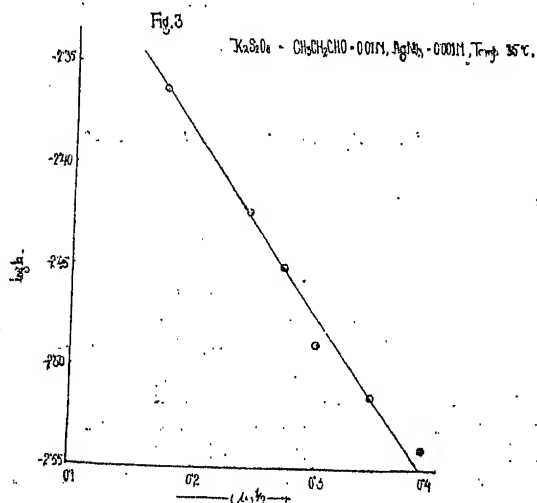
Specific Ionic Effect :—In order to determine the specific effect of ions, the reaction was studied at constant ionic strength in presence of different salts, the results of which are summarised below :—

TABLE 6

$\text{K}_2\text{S}_2\text{O}_8 = \text{CH}_3\text{CH}_2\text{CHO} = 0.01 \text{ M}$; $\text{AgNO}_3 = 0.001 \text{ M}$; Temp. 35°C .
 $\mu = 0.06$.

Salt added	Conc. of added salt	Mean $k \times 10^3$ (unimolecular)
No salt	($\mu = 0.03$)	4.3244
K_2SO_4	0.01 M	3.7741
Na_2SO_4	0.01 M	3.8392
MgSO_4	0.0075 M	4.3628
$(\text{NH}_4)_2\text{SO}_4$	0.01 M	4.5824
MgSO_4	0.01 M ($\mu = 0.09$)	3.8669

From the above results it is seen that the specific effect of K^+ is the greatest. In presence of Mg^{++} there is no perceptible change in the rate at the same ionic



strength. However, at higher ionic strength the rate slightly decreases. From the above data it may be concluded that the specific ionic effect is in the order $K^+ > Na^+ > Mg^{++} > NH_4^+$. In presence of NH_4^+ the rate increases instead of decreasing, as it should, in view of the negative salt effect. This increase in rate may be due either to the catalytic effect of NH_4^+ or due to the decomposition of persulphate ion by NH_4^+ (cf. the results of King⁵ on Ag^+ catalysed $S_2O_8^{--} - NH_4^+$ reaction).

Effect of H^+ ion:—To find out the effect of H^+ ion the reaction was studied in presence of H_2SO_4 and HNO_3 in two different experiments at the same ionic strength. For comparison the reaction was studied at the same ionic strength by the addition of the required amount of K_2SO_4 . Further, the reaction was carried out in the presence of a high concentration of K_2SO_4 , first in the absence of H_2SO_4 and then in the presence of H_2SO_4 so that the effect of H^+ ions may be correctly evaluated. The results of the above experiments are summarised below.

TABLE 7

$C_6H_5CHO = K_2S_2O_8 = 0.01 M ; AgNO_3 = 0.001 M ;$
 Temperature = $40^\circ C.$

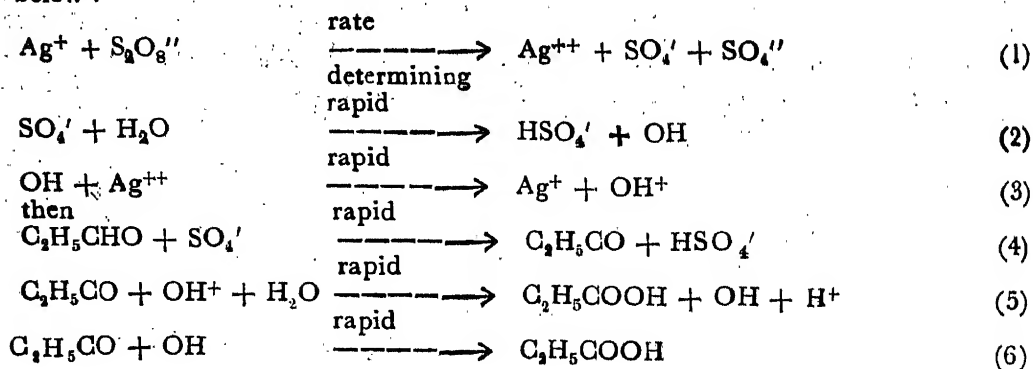
Conc. of added K_2SO_4	Conc. of acid added	Ionic strength of the reaction mixture	Mean value of k uni. $\times 10^3$
—	—	—	6.1558
—	$H_2SO_4 = 0.01 M$	0.06	4.9345
—	$HNO_3 = 0.03 M$	0.06	4.9444
$K_2SO_4 = 0.01 M$	—	0.06	4.7317
$K_2SO_4 = 0.1 M$	—	0.33	3.2865
$K_2SO_4 = 0.1 M$	$H_2SO_4 = 0.01$	0.36	3.1773

A close examination of the above data clearly shows that there is no perceptible effect of H ions on this reaction.

Effect of Ag⁺ ions.—In order to determine the effect of the concentration of the catalyst i.e. AgNO₃, the rate of the reaction was studied in the presence of different concentrations of AgNO₃. It was found that the rate increases in a linear manner with an increase in the concentration of the catalyst AgNO₃. This indicates that

the rate is linearly related to the AgNO₃ concentration i.e. $\frac{dx}{dt} \propto C_{Ag^+}$

*Discussion :—*Thus we find that the Ag⁺ catalysed reaction between potassium persulphate and propionaldehyde is unimolecular with respect to S₂O₈²⁻ and zero molecular with respect to propionaldehyde and exhibits a negative exponential salt effect. A comparison of the results with those obtained in the case of oxidation of formaldehyde and acetaldehyde (*loc. cit.*) shows that the rate constant for propionaldehyde oxidation is lower than that for the lower aldehydes, as it should be. Beside this, the reaction in each case is unimolecular, has a negative exponential salt effect, has the same order of the frequency factor value and the entropy of activation for all these oxidation reactions has a large negative value. These facts lead us to conclude that the Ag⁺ catalysed oxidation of all these aldehydes by persulphate ion follow a similar mechanism and the erratic and slightly abnormal results in the case of formaldehyde oxidation are due to its polymerisation. On the basis of our results summarised above, we are led to believe that the rate determining step is the reaction between two oppositely charged ions. Further we have shown in our previous paper⁶ that the product obtained in this reaction is propionic acid. The Ag⁺ catalysed reaction, therefore, probably follows the mechanism as outlined below :—



ACKNOWLEDGEMENTS

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REFERENCES

1. Khulbe, K. C. and Srivastava, S. P., *Agra Univ. Journal of Research (Science)*, **9**, 177 (1960).
2. Khulbe, K. C. and Srivastava, S. P., *Proc. Nat. Acad. Sci. (India)*, **32A**, 60 (1962).
3. Khulbe, K. C. and Srivastava, S. P., *Proc. Nat. Acad. Sci. (India)*, **30A**, 117 (1961).
4. Szabo, Cyanyi and Galiba, *Z. anal. Chem.*, **135**, 269 (1952).
5. King, C. V., *J. Amer. Chem. Soc.*, **49**, 2689 (1927); **50**, 2080 (1928); **52**, 1493 (1930).
6. Khulbe, K. C. and Srivastava, S. P., *Agra University Journal of Research (In Press)*.

PHYSICO-CHEMICAL STUDY OF THE COMPLEX FORMATION OF
BERYLLIUM IONS WITH ORGANIC LIGANDS. PART V.
WITH TARTARIC ACID AND ITS DERIVATIVES

By

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ABSTRACT

Beryllium sulphate is found to form 1:1 complexes with tartaric acid, sodium tartarate and malic acid. The complex formation has been studied by the electrical conductance, potentiometric measurements and by spectrophotometry in the ultra-violet region, using the method of continuous variations. The value of the dissociation constants of all these complexes are 10.65×10^{-4} for tartaric acid, 10.35×10^{-4} for sodium tartarate and 10.96×10^{-4} for malic acid respectively at 28°C.

In a number of earlier communications¹⁻⁵ several complexes of beryllium sulphate with a wide variety of organic ligands have been reported by the author. The only reference found in the literature⁶ is that sodium tartarate has been employed to study the system beryllium tartarate and evidence has been given for the formation of $\text{BeC}_4\text{H}_4\text{O}_6$ together with basic salts which are derivative of $\text{Be}(\text{OH})_2$.

The present communication deals with the studies on the complex formation of beryllium sulphate with tartaric acid, sodium tartarate and malic acid by physico-chemical methods like conductance, pH and spectrophotometry.

EXPERIMENTAL

An E. Merck sample of beryllium sulphate was taken and analysed. The analysis corresponded to the formula, $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ B.D.H. AnalaR samples of tartaric acid, sodium tartarate and malic acid were used for all purposes. Standard solutions were prepared from these substances in double distilled water. All the measurements were carried out in an electrically maintained thermostat at a constant temperature of $28 \pm 0.1^\circ\text{C}$.

Conductivity measurements were performed by a Doran's conductivity bridge with WTW Oscillator, while the pH measurements were carried out by means of a Beckmann pH meter (mains operated) with standard calomel electrode and glass electrode. The spectrophotometric measurements were done by a Beckmann D.U. spectrophotometer in the ultra-violet region using matched corex quality cells.

Stoichiometry of the components :

The composition of the complexes were determined by the Job's method of continuous variation.⁷ Equimolecular solutions of beryllium sulphate and the

organic ligands were used for this purpose. The divergence from the additivity rule was plotted against the ratio $(R)/(R) + (M)$, where (R) stands for the concentration of the ligand and (M) stands for that of the metal ion. The difference in conductivity, hydrogen ion concentration and optical density were plotted for electrical conductance, pH and spectrophotometric data respectively. For brevity, the graphs for spectrophotometry only with one concentration each have been incorporated in the present paper for tartaric acid (vide figs. 1-3). Similar graphs

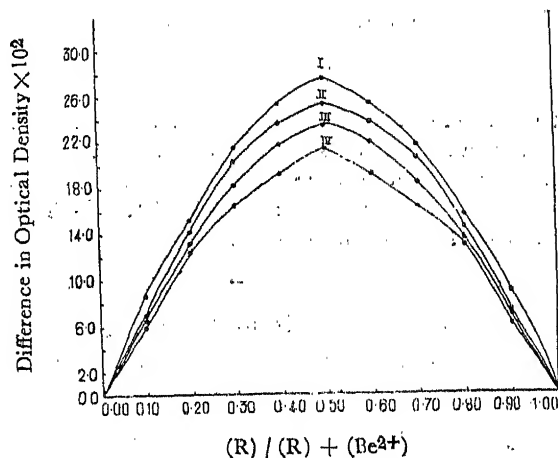


Fig. 1. Spectrophotometric Study of Be^{2+} - c Acid (Stoichiometry)

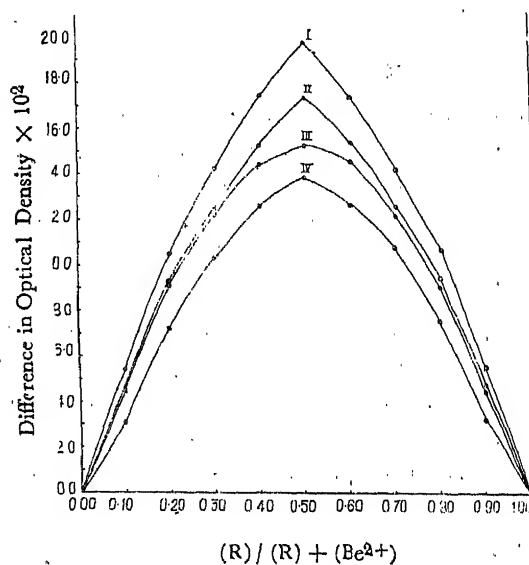


Fig. 2 Spectrophotometric Study of Be^{2+} - Sodium Tartarate (Stoichiometry)

or pH data and conductometric data have been omitted. From all these graphs it is seen that maxima are obtained at 0.50, which clearly proves the existence of 1:1 complexes in all the cases. Therefore it is established that beryllium sulphate forms 1:1 complexes each with tartaric acid, sodium tartarate and malic acid.

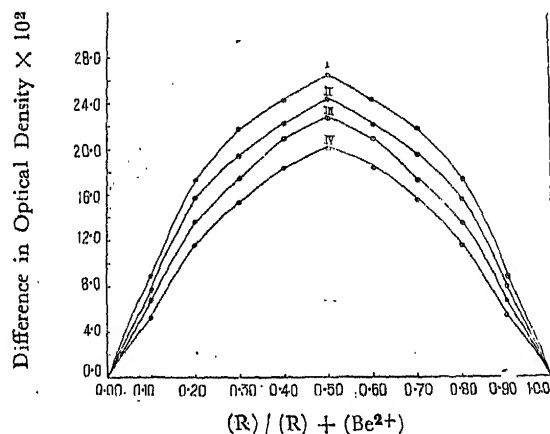


Fig. 3. Spectrophotometric Study of Be^{2+} - Malic Acid (Stoichiometry)

Value of dissociation constant :

Job's method (*loc. cit.*) has been employed to find the value of the dissociation constant of the complexes formed. Similar sets of solutions were prepared just as in the above case, the only difference being that non-equimolecular solutions have been employed in the present case. Since 1:1 complex has been established by all the three methods for different concentrations of the ligands, the Job's enlarged equation reduces to the following as $m = 1$ and $n = 1$.

$$K = \frac{c [(p + 1)x - 1]^2}{(p - 1)(1 - 2x)},$$

where c stands for the concentration of beryllium ions, x stands for the amount of ligand used up and p stands for the ratio of the concentration of the ligand and that of the metal solution. In this case also the divergence from the additivity rule has been plotted against the amount of the ligand used up. For brevity, the graphs for spectrophotometry only with one concentration each have been incor-

porated in the present communication for tartaric acid (vide Figs. 4-6). Similar graphs for the pH data and conductivity data have been omitted. The values of

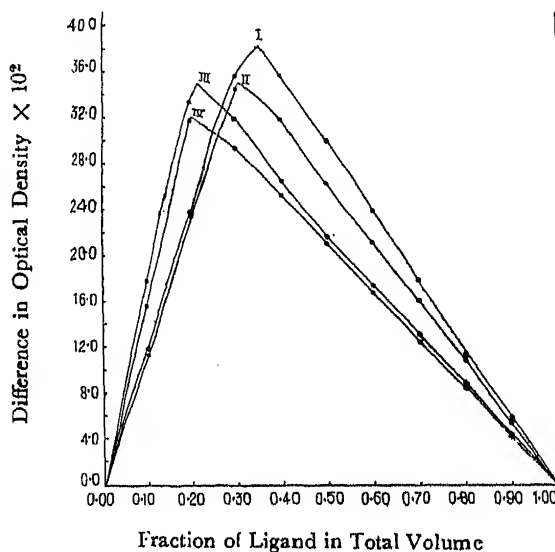


Fig. 4. Spectrophotometric Study of Be^{2+} - Tartaric Acid (Dissociation Constant)

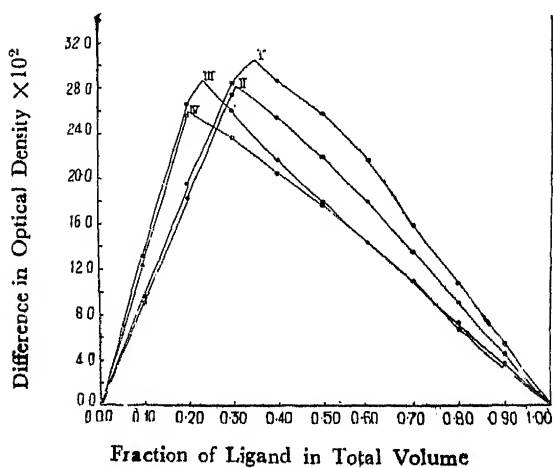


Fig. 5. Spectrophotometric Study of Be^{2+} - Sodium Tartarate (Dissociation Constant)

the dissociation constants for different concentrations of tartaric acid, sodium tartarate and malic acid measured at 28°C, as calculated from the above equation of Job, have been recorded in tables I, II & III, respectively.

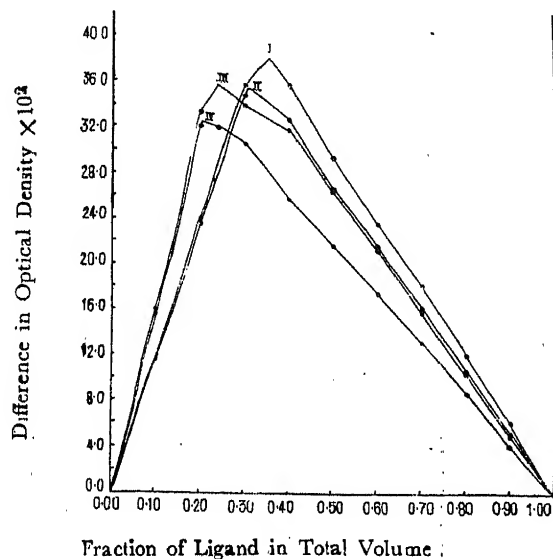


Fig. 6. Spectrophotometric Study of Be^{2+} -Malic Acid
(Dissociation Constant)

TABLE I

Fig. No.	Curve No.	c	p	x	$K \times 10^4$
4	I	0.10	2.0	0.352	10.72
4	II	0.10	2.5	0.308	10.69
4	III	0.05	4.0	0.237	10.60
4	IV	0.05	5.0	0.204	10.59

Average value = 10.65×10^{-4}

TABLE II

Fig. No.	Curve No.	c	p	x	$K \times 10^4$
5	I	0.10	2.0	0.352	10.44
5	II	0.10	2.5	0.308	10.39
5	III	0.05	4.0	0.236	10.30
5	IV	0.05	5.0	0.203	10.27

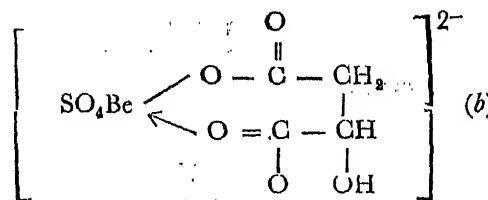
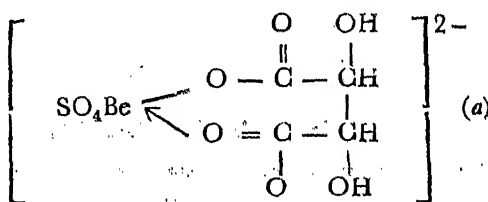
Average value = 10.35×10^{-4}

TABLE III

Fig. No.	Curve No.	c	p	x	$K \times 10^4$
6	I	0.10	2.0	0.352	11.07
6	II	0.10	2.5	0.308	10.99
6	III	0.05	4.0	0.238	10.91
6	IV	0.05	5.0	0.205	10.87

Average value = 10.96×10^{-4}

The following structures are tentatively assigned to the tartaric acid and sodium tartarate (a) and malic acid (b) complexes.



The above structures (a) and (b) satisfy the coordination maximum of beryllium which is four.

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REFERENCES

1. Bhattacharya, Arun K., et. al., *Curr. Sci.*, 28, 241 (1959).
2. Bhattacharya, Arun K., et. al., *J. Sci. Ind. Res.*, 18, 351 (1959).
3. Bhattacharya, Arun K., et. al., *J. Uni. Saug.*, 8, 21 (1959).
4. Bhattacharya, Arun K., et. al., *Proc. Nat. Acad. Sci. India*, 29A, 76 (1960).
5. Bhattacharya, Arun K., et. al., *Z. phys. Chem.*, 219, 11 (1952).
6. Zolotukhin, K.E., *Zhur. Neorg. Khim.*, 1, 2676 (1956).
7. Job, P., *Comp. rend.*, 180, 928, (1928).

ON STEADY GAS FLOWS

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ABSTRACT

Assuming the equation of state for a gas as $f(P, \rho, s) = 0$ and using vector methods we observe that the coincidence of isovels with streamlines implies also the coincidence of iso-bars, iso-therms, isopycnics and equienthalpy lines with them. A result obtained by Kapur [1].

In the case of plane gas flows iso- curls also coincide with them. Choosing streamlines as one set of orthogonal curvilinear coordinate curves and using again vector methods, we have shown by a simple and more elegant way than Kapur's [1] that the streamlines in the above case are either concentric circles or parallel straight lines. We have also shown that when velocity magnitude is constant throughout the region the motion need not be irrotational. c.f. incompressible [3]. If such a flow is irrotational pressure also is uniform.

We find that the necessary and sufficient condition for a plane gas flow to be barotropic, is the coincidence of the above curves. This condition further is equivalent to coincidence of streamlines with iso-vels or iso-bars or isopycnics.

1. BASIC EQUATIONS

The basic equations governing a steady flow of perfect gas are given below in the usual notation :

Equation of continuity:

$$(1) \quad \text{Div} (\rho \vec{q}) = 0$$

Momentum equation:

$$(2) \quad \text{Curl } \vec{q} \wedge \vec{q} + \text{grad } \frac{q^2}{2} + 1/\rho \text{ grad } P = 0$$

State equation:

$$(3) \quad f(P, \rho, s) = 0$$

Gas equation:

$$(4) \quad P = \rho R T.$$

Energy :

$$(5) \quad \vec{q} \cdot \text{grad } s = 0$$

Equation of enthalpy :

$$(6) \quad q^2 + 2h(P, s) = a^2 = 2h(P_0, s).$$

Where

$$h(P, s) = \int_0^P \frac{dp}{\rho(P, s)}$$

Crocco's vortex equation

$$(7) \quad \vec{q} \wedge \text{Curl } \vec{q} = \text{grad } (h + q^2/2) - T \text{ grad } s$$

§ 2. (A)

In this section it is proposed to derive some of the properties of gas flows whose iso-vels coincide with stream lines i. e.

$$(8) \quad \vec{q} \cdot \text{grad } q = 0$$

Taking the scalar product of (2) by \vec{q} and using (8) we obtain

$$(9) \quad \vec{q} \cdot \text{grad } P = 0$$

Hence it follows from (5), (9) and (3)

$$(10) \quad \vec{q} \cdot \text{grad } \rho = 0$$

Again taking the scalar product of (7) by \vec{q} and using (5) and (8) we obtain

$$(11) \quad \vec{q} \cdot \text{grad } h(p, s) = 0$$

From (9) and (10) together with (4) it follows that the stream lines are iso-therms.

Operating curl on (2) we get

$$\text{Curl } (\vec{\zeta} \wedge \vec{q}) + \text{grad } (1/\rho) \wedge \text{grad } P = 0$$

By virtue of (9) and (10), this reduces to

$$(12) \quad \text{Curl } (\vec{\zeta} \wedge \vec{q}) = 0$$

From (8) to (12) we observe that when iso-vels coincide with stream lines, iso-bars, iso-therms, iso-pyenics and equi-enthalpy lines all coincide with stream lines. For a plane flow, isocurls also coincide with them.

(B). We shall also prove that the above results hold good, for a barotropic fluid ($P = P(\rho)$).

Taking gradient of the equation (3) we get

$$(13) \quad \left[\frac{\partial f}{\partial P} \cdot \frac{\partial P}{\partial \rho} + \frac{\partial f}{\partial \rho} \right] \text{grad } \rho + \frac{\partial f}{\partial s} \cdot \text{grad } s = 0$$

Multiplying scalarly by \vec{q} and using (5) we get either

$$(14) \quad \vec{q} \cdot \text{grad } \rho = 0 \quad \text{or} \quad \frac{\partial f}{\partial \rho} \cdot \frac{d\rho}{d\rho} + \frac{\partial f}{\partial \rho} = 0$$

Since we are dealing with iso-entropic gases, we reckon only the former equation of (14) i. e. iso-pycnics coincide with stream lines, and hence iso-bars also.

Taking the scalar product of (2) by \vec{q} and using the condition of coincidence of iso-bars with streamlines we get

$$(15) \quad \vec{q} \cdot \text{grad } q^2/2 = 0$$

Hence it follows that if a gas is barotropic, streamlines, iso-vels, iso-curls, iso-bars, iso-pycnics, iso-therms and equienthalpy lines all coincide converse is also true. For a plane flow isocurles also coincide with them.

§ 3. PLANE GAS FLOWS

(A) In the plane we shall choose orthogonal curvilinear co-ordinate system : $\alpha(x, y) = \text{constant}$ as streamlines and $\beta(x, y) = \text{constant}$ as their orthogonal trajectories. $h_1(\alpha, \beta) d\alpha$ and $h_2(\alpha, \beta) d\beta$ are the components of the vector lengths of are ds .

Then we have

$$(16) \quad \vec{q} = e_\beta \cdot q.$$

Where e_β is unit-vector in the β direction.

and

$$(17) \quad \zeta = \text{Curl } \vec{q} = \frac{q}{h_1} \frac{\partial}{\partial \alpha} [\log(h_2 q)].$$

Which is perpendicular to the α - β plane.

Then (1) reduces to

$$(18a) \quad \frac{\partial}{\partial \beta} (h_1 \rho q) = 0$$

$$\text{i. e. (18b)} \quad h_1 \rho q = H(\alpha)$$

Equation (2) gives

$$(19) \quad -q \zeta + \frac{1}{h_1} \frac{\partial}{\partial \alpha} (q^2/2) + \frac{1}{\rho h_1} \frac{\partial P}{\partial \alpha} = 0$$

$$\text{and (20)} \quad \frac{\partial}{\partial \beta} (q^2/2) + \frac{1}{\rho} \frac{\partial P}{\partial \beta} = 0$$

Lame's condition [4]

$$(21) \quad \frac{\partial}{\partial \alpha} \left[\frac{1}{h_1} \frac{\partial h_2}{\partial \alpha} \right] + \frac{\partial}{\partial \beta} \left[\frac{1}{h_2} \frac{\partial h_1}{\partial \beta} \right] = 0$$

If τ is the radius of curvature of the streamline we have

$$(22) \quad \frac{1}{\tau} = \text{Div} \left[\frac{\text{grad } \alpha}{|\text{grad } \alpha|} \right] = \frac{1}{h_1 h_2} \frac{\partial h_2}{\partial \alpha}$$

Eliminating P and $q^2/2$ from (19) and (20), and using (18b) we get respectively

$$(23) \quad -H(\alpha) \frac{\partial \xi}{\partial \beta} + \frac{\partial (q^2/2, \rho)}{\partial (\alpha, \beta)} = 0$$

and

$$(24) \quad -H(\alpha) \frac{\partial}{\partial \beta} (\xi/\rho) + \frac{\partial (P, 1/\rho)}{\partial (\alpha, \beta)} = 0$$

When iso-vels coincide with streamlines (12) reduces to

$$(25) \quad \frac{\partial}{\partial \beta} \left[q^2 \frac{\partial}{\partial \alpha} (\log h_2 q) \right] = 0$$

and equation (18a) gives

$$(26) \quad \frac{\partial h_1}{\partial \beta} = 0 \text{ i.e. } h_1 = h_1(\alpha)$$

(25) then yields

$$(27) \quad h_2 = h(\alpha) g(\beta).$$

Substituting (26) and (27) in (21) we obtain

$$(28) \quad \frac{dh}{d\alpha} = c h_1(\alpha)$$

Where 'c' is an arbitrary constant.

Using (26), (27) and (28) in (22) we obtain

$$(29) \quad \frac{1}{\tau} = \frac{c}{h(\alpha)}$$

Hence it follows that τ is a function of ' α '; the streamlines are concentric circles, and when h_2 is a function of β alone they become parallel straight lines. This result was obtained by Kapur [1] and also by Nemenyi and Prim [2] but our method is simple and elegant.

(B). Consider the case when the velocity in magnitude is constant throughout the region of flow and iso-pycnics coincide with stream lines, and equations (26), (27) and (28) remain the same.

In this case (17) reduces to:

$$(30) \quad \text{Curl } \vec{q} = \frac{q}{h_1 h_2} \frac{\partial h_2}{\partial \alpha} = \frac{cq}{h(\alpha)}$$

So the flow need not be irrotational, when the velocity is constant throughout the region. This is in contrast to an incompressible plane flow which becomes irrotational when the velocity is constant throughout the region [3].

If the compressible flow with constant velocity should be irrotational (17) shows that h_2 is independent of ' α '. (22) shows that the stream lines in this case are straight lines. Equations (19) and (20) show that pressure for such a flow is uniform throughout. In this case iso-pycnics and iso-therms are identical with stream lines.

(C) Suppose q is not constant throughout, but the flow is irrotational.

Operating curl on (2) we get

$$(31) \quad \text{grad } (1/\rho) \wedge \text{grad } P = 0$$

and

$$(32) \quad \text{grad } \rho \wedge \text{grad } q^{1/2} = 0$$

From (4), (31) and (32) we conclude that iso-bars, iso-pycnics, iso-vels and iso-therms coincide. They can remain different from streamlines.

§ 4. CONFLUENCE OF CURVES AND BARATROPY.

In this section we shall examine if the fluid is barotropic when two of the following curves coincide:—

Streamlines, iso-vels, iso-curls, iso-pycnics, and iso-bars.

The case when stream lines and iso-vels coincide has been considered in § 2.

(A) When iso-curls and stream lines coincide, (23) and (24) respectively reduce to

$$(33) \quad \frac{\partial (q^{1/2}, \rho)}{\partial (\alpha, \beta)} = 0$$

and

$$(34) \quad h_1 q \zeta(\alpha) \frac{\partial}{\partial \beta} \log \rho + \frac{\partial (P, 1/\rho)}{\partial (\alpha, \beta)} = 0$$

(33) shows that iso-vels coincide with iso-pycnics, but the fluid need not be barotropic.

But Nemenyi and Prim [2] have proved that coincidence of iso-curls with stream lines implies the coincidence of iso-vels with stream lines, i. e. the fluid is barotropic; they have assumed the product equation of state.

(B) When iso-bars coincide with iso-vels, (23) and (24) respectively reduce to

$$(35) \quad -H(\alpha)\xi + \frac{\partial p}{\partial \alpha} \left[\rho q \frac{dq}{dp} + 1 \right] = 0$$

$$\text{and (36)} \quad \frac{\partial p}{\partial \beta} \left[\rho q \frac{dq}{dp} + 1 \right] = 0$$

Therefore either (i) $\frac{\partial p}{\partial \beta} = 0$ or (ii) $\rho q \frac{dq}{dp} + 1 = 0$

In the first case either p is uniform or constant only on streamlines. When P is uniform velocity magnitude is constant throughout, motion irrotational, and streamlines become straight lines. Also when P is constant on individual streamlines, motion can be rotational or irrotational and fluid is barotropic.

In the second case $\rho(P) = -\frac{1}{q(P) \cdot \frac{dq}{dP}}$, motion is irrotational and the

fluid is barotropic.

Again from (23) and (24) it can be seen that the fluid need not be barotropic when iso-curves coincide with iso-pycnics (excluding the case when $\xi = a\rho + b$) or iso-vels or iso-bars. The same is found when iso-vels coincide with iso-pycnics.

Hence we find that only when streamlines coincide with isovels or iso-pycnics or with iso-bars, the plane gas flow is barotropic and the stream lines are either concentric circles or parallel straight lines.

REFERENCES

1. Kapur, J. N., *Proc. Nat. Inst. Sci. India*, 28, 457 (1962).
2. Naményi and Prim, *J. Phys. and Maths, Mass. Inst. Tech.*, 28, 130 (1948).
3. Purushotham, G., *Proc. Nat. Acad. Sci., India* (In Press).
4. Weatherburn, C. E., *Differential Geometry of three Dimensions*, Camb. Univ. Press., p. 214 (1955).

DIURNAL VARIATION OF COSMIC RAY INTENSITY AT GULMARG

($\lambda = 24.7^\circ\text{N}$)

By

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[Received on 21st March, 1963]

ABSTRACT

The result presented in this paper concern the study of the diurnal variation of hard component of cosmic-rays at Gulmarg ($\lambda = 24.7^\circ\text{N}$, 9000 ft.) during I. G. Y. (1958), using three narrow angle telescopes having semi-angles 4° , 7° , and 14.5° , in the N-S plane and a semi-angle of 45° , for each in the E-W plane in addition to the cubical meson-telescope.

Comparative study of the diurnal variation shows that the amplitude of the diurnal variation increases as the aperture of the telescope decreases.

INTRODUCTION

Measurements of the intensity of cosmic-radiation have shown that there is a Solar time diurnal variation with an amplitude less than 1% (Progress in cosmic-ray Physics 1952)¹. Large amplitudes of the Solar diurnal variation of meson intensity, observed by means of narrow angle telescopes by Japanese group and other workers² encouraged the author to perform this type of study at Gulmarg ($\lambda = 24.7^\circ\text{N}$, 9000 ft.) with different narrow-angle telescopes.

Thus, at Gulmarg during the year 1958 diurnal variation of meson intensity was studied, using three narrow-angle telescopes having semi-angles of 4° , 7° , and 14.5° in the N-S plane and a semi-angle of 45° for each in the E-W plane in addition to the cubical meson telescope.

ANALYSIS OF THE DATA AND RESULTS

The data corrected for barometric pressure was smoothed by taking moving averages over three consecutive bihourly values, the average value thus centered at the middle hours. The final values are obtained by adding smoothed values for the same bihourly interval for all the days from Feb. to December, 1958. The amplitude and phase of the diurnal and semi-diurnal components of the daily variation of meson intensity measured with different narrow-angle telescopes are given in the table (1) and are also represented on harmonic dial in fig. 2.

From the table (1) it is observed that :

TABLE-1

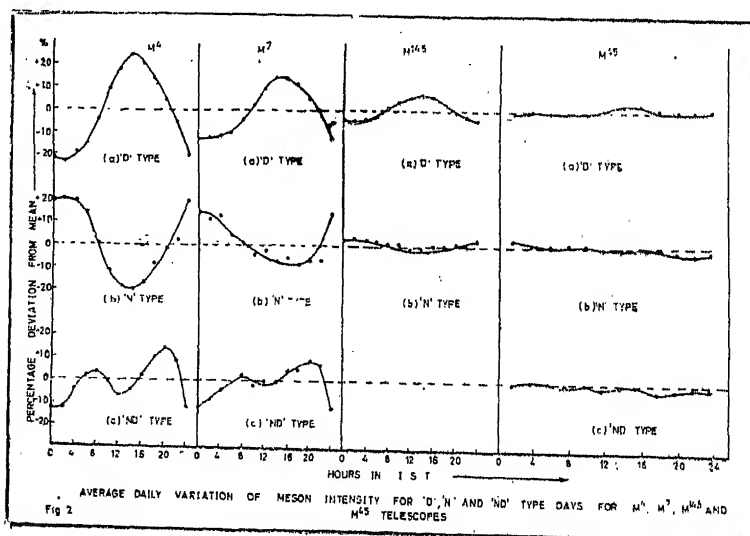
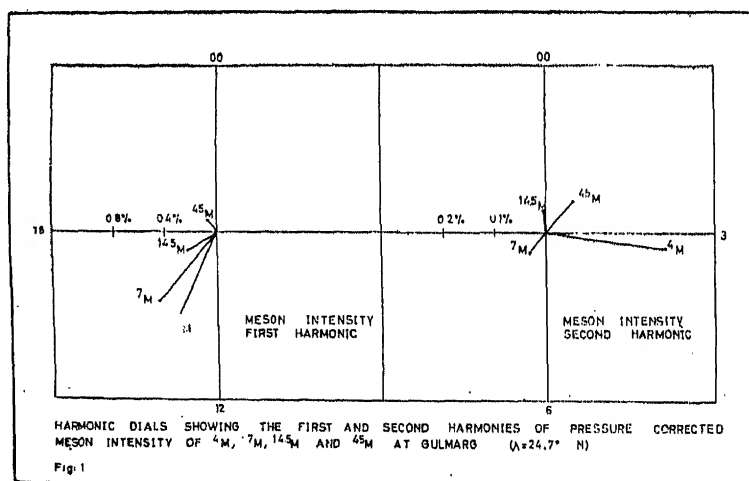
The percentage amplitude and the Phase of the first and the second Harmonics of the daily variation of meson intensity measured with different telescopes of Semi-Angles 4° , 7° , 14.5° , and 45° (Cubical telescope)

Semi-angle in N-S plane	S. D. %	First Harmonic			Second Harmonic		
		Amplitude	Phase	in ϕ_G^D I. S. T.	Amplitude	Phase	in ϕ_G^S I. S. T.
		M_G^D	ϕ_G^D		M_G^S	ϕ_G^S	
		%			%		
4°	± 0.14	0.75	205°	1340 hrs.	0.23	52°	0328 hrs.
7°	± 0.09	0.70	221°	1444 hrs.	0.05	129°	0836 hrs.
14.5°	± 0.05	0.28	239°	1556 hrs.	0.04	178°	1152 hrs.
45°	± 0.01	0.12	324°	2136 hrs.	0.08	42°	0248 hrs.

TABLE-2

Comparative study of the Amplitude and Phase of the first Harmonic component with different telescopes having semi-angles of 4° , 7° , 14.5° , and 45° in the N-S plane

Semi-angle in N-S plan	S. D. %	First Harmonic			Phase			Difference
		$M_G^D(D)$	$M_G^D(N)$	$M_G^D(ND)$	$\phi_G^D(D)$	$\phi_G^D(N)$	$\phi_G^D(ND)$	$\phi_G^D(D) - \phi_G^D(N)$
		%	%	%				
4°	± 0.20	2.30	2.07	0.53	232°	56°	182°	176°
7°	± 0.12	1.39	0.96	0.48	221°	39°	205°	182°
14.5°	± 0.07	0.57	0.20	...	245°	48°	...	197°
45°	± 0.02	0.15	0.13	0.10	233°	347°	183°	246°



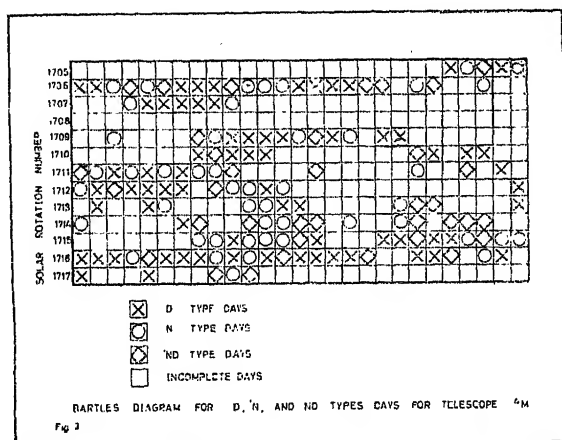
- (1) the amplitude of the first harmonic component becomes larger as the aperture of the telescopes becomes smaller.
- (2) the time of maximum ϕ^D of the diurnal component corresponding to about 1340 hrs., 1444 hrs., 1556 hrs., and 2136 hrs., in I. S. T. for 4M , 7M , $^{14.5}M$ and ^{45}M respectively. This shows that the time of maximum of the diurnal component increases as the aperture of the telescope becomes wider.
- (3) the phase ϕ^S of the semi-diurnal component also increases as the aperture of the telescope becomes wider.

DAY TO DAY CHANGES IN THE DIURNAL VARIATION OF COSMIC/RAY INTENSITY

For a physical interpretation of the solar anisotropy of cosmic-rays, in the context of great variability, it is important to examine the distinctive forms of the daily variation that occur on individual days. Often, however, the standard error of an experimental determination of the daily variation of an individual day is too large to permit valid conclusions, and data are then averaged over a number of days grouped together on some criteria. The study of day to day changes of the anisotropy at Gulmarg was performed by using the method suggested by Sittkus (1955)³ as well as by Remy and Sittkus (1955)⁴. Thus following their method the daily variation are designated 'D' type having maxima in day-time, 'N' type having a maxima in night-time, and 'ND' type having two maxima on a particular day.

If on a day the time of maxima occur between 0800 and 2000 hrs. I. S. T., it is called a 'D' type daily variation on that day and when the time of maxima occurs between 2000 and 0800 hrs, it is a 'N' type daily variation. Similarly the days with two maxima one between (800 and 2000 hrs., and the other between 2000 and 0800 hrs., are designated as 'ND' type. All these types of daily variation are put into three groups 1st., 2nd., and 3rd. respectively.

For the telescope $^{14.5}M$, the number of days of 'ND' type being very small and therefore the standard error is quite large, are left out of consideration. The amplitude and phase of the diurnal variation of meson intensity for different type of groups for telescopes having semi-angles 4° , 7° , 14.5° and 45° in the N-S plane, according to their classification, are given in the table (2). In figure 3, the curves



show separately the daily variation for telescopes 4^3M , 7^3M , 14.5^3M and 45^3M for all days on which;

- (a) there is a significant 'D' type daily variation.
- (b) there is a significant 'N' type daily variation. (in this case the peak of maxima is not well defined) and
- (c) there is a significant 'ND' type of daily variation (in this case the two peaks are not well defined for telescope 45^3M)
- (d) The difference of phase $\phi(\text{D}) - \phi(\text{N})$ increases as the aperture of the telescopes becomes wider.

For the telescope of aperture 4^3 the percentage of occurring of the 'D', 'N', and 'ND' type of days is 48.2%, 27.3%, and 24.5% respectively. This shows that the 'D' type daily variation is more frequent at Gulmarg than other types discussed here. This type of result was also observed by Ch. V. Sastry⁵ in case of neutron intensity at Gulmarg.

Fig. (4) shows the Barte's diagram for 'D', 'N', and 'ND' type of days. Those days for which the data are either not available or incomplete for evaluating the diurnal variation are also indicated on the diagram. It may be seen from the diagram that there is a tendency for 'D', 'N' and 'ND' type to occur in groups of days and it is more prominent in case of 'D' and 'N' type of days. Though not very clear from the fig. (4), but the evidence is also seen for 27-day recurrence tendency in case of 'D' and 'N' type of days.

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REFERENCES

1. Elliot, H., Progress in Cosmic-Ray Physics, vol. 1 (1952).
2. Sekido, Y., Kodama, M. and Yagi, T., *Rep. Ionosphere, Res., Japan*, 4, 207 (1950).
3. Sittkus, A., *J. Atmos. Terr. Phys.*, 7, 80 (1955).
4. Remy, E. and Sittkus, A., *Z. Naturforsch.*, 10a, 172 (1955).
5. Ch. V. Sastry, Ph. D. Thesis, Muslim University, Aligarh (1960).

STUDIES IN ALKYL ESTERS OF 1-HYDROXY PHOSPHONIC ACID-PART I

By

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ABSTRACT

A number of new analogues of O, O dimethyl 2, 2, 2, trichloro 1-hydroxy phosphonate (Dipterex) have been synthesised by condensing 3, 4 dimethoxy benzaldehyde, and 3, 4 dimethoxy-6-nitro-benzaldehyde with dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl diisoamyl, and tdi-sec-amyl phosphites in presence of sodium methylate catalyst.

The compounds synthesised from 3, 4 dimethoxy benzaldehyde are coloured liquids of high specific gravity and those synthesised from 3, 4 di-methoxy-6-nitro benzaldehyde are coloured solids with definite melting points.

In recent years a considerable amount of work has been done on condensation reaction of dialkyl hydrogen phosphites with aldehydes and ketones to form esters of 1-hydroxy phosphonic acid. Abramov, Pudovik and others^{1,2} described this condensation reaction in which they have used lithium or sodium methylate as catalyst for condensing a series of aliphatic and few aromatic aldehydes and ketones. Fields³ obtained a process patent on this reaction using triethylamine as catalyst.

Barthel, Giang and Hall⁴ condensed chloral with dimethyl-diethyl-dipropyl-diisopropyl-and dibutyl phosphites without any catalyst to obtain compounds, which proved good insect poisons. O, O dimethyl, 2, 2, 2 trichloro 1-hydroxy ethyl phosphonate has been found effective against D. D. T. resistant House flies.⁵

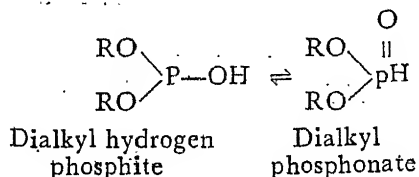
In an attempt for a search for new organic phosphorus insecticides, a series of new O, O dialkyl 1-hydroxy phosphonates have been prepared by consensing 3, 4-dimethoxy benzaldehyde and 3, 4-dimethoxy-6-nitro benzaldehyde with dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, diisoAmyl and di-secamyl phosphites and characterised as detailed in the experimental part.

The catalyst employed in these condensations was sodium-methylate (saturated). Other catalysts like sulphuric acid, sodium ethoxide were also tried, but encouraging results were obtained by using sodium methylate.

EXPERIMENTAL

Dialkyl Hydrogen Phosphites:—These were prepared from phosphorus trichloride and corresponding alcohols by the method of H. McCombie, *et al*^{6,7} using carbon-tetrachloride as a solvent.

The physical properties and yields are as follows.



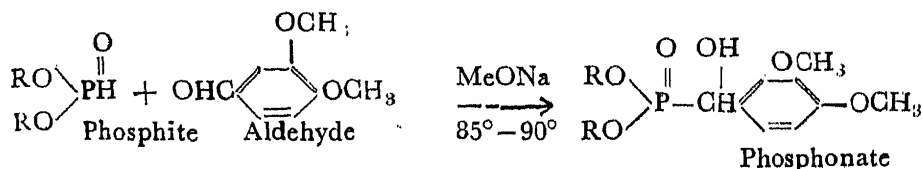
R	B.P°C	Pressure/mm	% Yield
1. Dimethyl	64-66	16	35
2. Diethyl	74-76	15	78.2
3. Diisopropyl	84-86	22	84
4. Dipropyl	110	10	69.8
5. Diisobutyl	105-107	12	86
6. Dibutyl	126-130	19	65.6
7. Di (1-ethyl- n-propyl)	112-115	9	71
8. Di (3-methyl- n-butyl)	124-127	13	68.9

Substituted Aldehydes:—

(1) 3, 4-dimethoxy benzaldehyde.—It was prepared by methylation^a of 3-methoxy 4-hydroxy benzaldehyde with dimethyl sulphate and alkali.

(2) 3, 4-dimethoxy-6-nitro benzaldehyde^o. It was prepared by nitration of 3, 4-dimethoxy benzaldehyde with nitric acid in absence of light.

O, O dialkyl-1-hydroxy (3, 4-dimethoxy phenyl) phosphonate.



*Method:—*Equimolar quantities of 3, 4-dimethoxy benzaldehyde and dialkyl hydrogen phosphite were mixed together and sodium methoxide was added drop by drop heat being evolved during the reaction. The mixture was shaken continuously till heat evolution had ceased. It required about 18-20 drops of sodium methoxide. The temperature of the mixture was raised and maintained at 85°-90°C for 20—25 minutes.

The reaction mixture was cooled, washed with water, dried over anhydrous sodium sulphate and distilled under low pressure.

The properties, yield and percentage of phosphorus in these new compounds are detailed in table 1.

O, O dialkyl-1-Hydroxy (3, 4-dimethoxy-6-nitro phenyl) phosphonate:—

Equimolar quantities of nitro-aldehyde and dialkyl hydrogen phosphite were condensed as described above under 3, 4-dimethoxy benzaldehyde.

Next day the reaction product was diluted with water. The precipitate was filtered, washed with water, dried and crystallised from hot absolute ethanol, tiny needles, which were filtered, washed with cold alcohol and dried.

The properties, yield and percentage of phosphorus determined by Pregl¹⁰ method are given in table 2.

TABLE I

Dialkyl- α -hydroxy phosphonates.

Name	Formula	% yield	State & Colour	B.P. °C/mm	% P found	% P Theo.
1. o, o dimethyl- α -hydroxy (3, 4-dimethoxy phenyl) phosphonate.	$C_{11}H_{16}O_6P$	65.2	Yellow Oil	161-164/12	10.94	11.2
2. o, o diethyl- α -hydroxy (3, 4-dimethoxy phenyl) phosphonate.	$C_{13}H_{20}O_6P$	93.4	red oil	152-156/14	10.32	10.19
3. o, o di-isopropyl- α -hydroxy (3, 4-dimethoxy phenyl) phosphonate.	$C_{15}H_{26}O_6P$	68.6	red oil	145-148/12	9.13	9.3
4. o, o dipropyl- α -hydroxy (3, 4-dimethoxy phenyl) phosphonate.	$C_{15}H_{26}O_6P$	84.3	red oil	137-139/13	9.51	9.3
5. o, o dibutyl- α -hydroxy (3, 4-dimethoxy phenyl) phosphonate.	$C_{17}H_{26}O_6P$	83.3	red oil	137-141/16	8.43	8.6
6. o, o diisobutyl- α -hydroxy (3, 4-dimethoxy phenyl) phosphonate.	$C_{17}H_{26}O_6P$	83.3	red oil	157-164/40	8.29	8.6
7. o, o di-(1-ethyl-n-propyl)- α -hydroxy (3, 4-dimethoxy phenyl) phosphonate.	$C_{19}H_{32}O_6P$	79.8	red oil	157-60/10	7.76	7.9
8. o, o di-(3-methyl-n-butyl)- α -hydroxy (3, 4-dimethoxy phenyl) Phosphonate.	$C_{19}H_{32}O_6P$	66.9	yellow oil	154-155/10	7.65	7.9

TABLE 2
Dialkyl- α -hydroxy phosphonates.

Name	Formula	% yield	Shape of crystal	Colour	M.P.°C	% P (found)	% P (Theo)
1. o, o dimethyl- α -hydroxy (3, 4-dimethoxy 6-nitro phenyl) phosphonate.	$C_{11}H_{18}O_8PN$	46.7	fine needles	dark yellow	201	8.9506	9.6
2. o, o diethyl- α -hydroxy (3, 4-dimethoxy-6-nitrophenyl) phosphonate.	$C_{13}H_{20}O_8PN$	20	needles	dark yellow	204	8.1532	8.9
3. o, o diisopropyl- α -hydroxy (3, 4-dimethoxy-6-nitrophenyl) phosphonate.	$C_{15}H_{24}O_8PN$	29.1	needles	yellow	melt with dec. at 192	8.0163	8.2
4. o, o dipropyl- α -hydroxy (3, 4-dimethoxy-6-nitrophenyl) phosphonate.	$C_{15}H_{24}O_8PN$	29.1	needles	yellow	melt with dec. above 195	7.8003	8.2
5. o, o dibutyl- α -hydroxy (3, 4-dimethoxy-6-Nitrophenyl) phosphonate.	$C_{17}H_{28}O_8PN$	29.6	needles	reddish yellow	231-232	7.3054	7.6
6. o, o diisobutyl- α -hydroxy (3, 4-dimethoxy-6-nitrophenyl) phosphonate.	$C_{17}H_{28}O_8PN$	29.6	needles	yellow	melt with dec. at 189-190	7.2735	7.6
7. o, o di (1-ethyl-n-propyl)- α -hydroxy (3, 4-dimethoxy-6-nitrophenyl) phosphonate.	$C_{19}H_{30}O_8PN$	24.2	needles	reddish yellow	186	6.7528	7.3
8. o, o di (3-methyl-n-butyl)- α -hydroxy (3, 4-dimethoxy-6-nitrophenyl) phosphonate.	$C_{19}H_{30}O_8PN$	18.5	needles	yellowish white	192	6.9304	7.3

The insecticidal activity of above compounds are under investigation.

REFERENCES

1. Abramov, V. S. *Doklady Akad. Nauk*, S. S. S. R., **73**, 487 (1950); *J. Gen. Chem. U. S. S. R.*, **22**, 647 (1952).
2. Pudovik, A. N., Arbuzov, A. E., *Doklady Akad. Nauk*, S. S. S. R., **73**, 499 (1950).
3. Fields, E. K., *U. S. Patent*, **2**, 579, 810 (1951).
4. Barthel, W. F., Giang, P. A. and Hall, S.A., *J. Amer. Chem. Soc.*, **76**, 4186 (1954).
5. Technical grade O, O-dimethyl, 2, 2, 2 Trichloro-1-hydroxy ethyl phosphonate has been designated as "L13/59" and supplied by Geary, R. J., Blue point, N. Y. for entomological tests.
6. McCombie, H., Saunders, B. C., and Stacey, G. J., *J. Chem. Soc.*, 380 (1945).
7. Cook, H. G., McCombie, H., and Saunders, B. C., *J. Chem. Soc.*, 873 (1945).
8. *Organic Synthesis*, Vol. II, 6th Edition (1950), Edited by A. H. Blatt, p. 619.
9. *Organic Synthesis*, Vol. 33, Edited by C. C. Price, 65 (1953).
10. *Micro-Analysis* by A. Steyermark, A., 1st Edition 8 (1951) p. 192.

EFFECT OF VARIOUS LEVELS OF NITROGEN WITH AND WITHOUT PHOSPHATES AND POTASH, ON THE OIL AND PROTEIN CONTENTS OF RAI (BRASSICA JUNCEA) SEEDS

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ABSTRACT

The effect of heavy nitrogenous fertilization with and without phosphatic and potassic fertilizers on Oil and protein contents of rai was studied. The dose of nitrogen varied from 0, to 160, lb per acre whereas the doses of phosphate and potash were kept at 40 lb per acre. The oil content decreased with the increased nitrogenous fertilization whereas phosphatic and potassic fertilizers increased it. The correlation between oil and protein contents were inversely proportional.

The effect of agronomical practices like seed rate, spacing, manuring and irrigation on the yield and quality of oil in oil seed crops is of considerable practical interest. Blackmann and Bunting (1951) observed slight depression in the oil content and increase in protein content of linseed by the addition of nitrogen whereas Sen and Sircar (1958) showed better oil content of Brassica juncea by phosphate. An increase in oil and decrease in protein contents were also observed by Bjorklund and Wahlgreen (1955) and Anderson *et. al* (1956) in oleiferous Brassicae. Sinha *et al* (1961) & 1962) noted that oil yield is depressed in yellow sarson and rai with nitrogen.

In agronomical experiments Brassica juncea (rai) R.T. 11 appeared in respect of yield to respond well to higher doses of nitrogen, phosphates and potash. Hence it was considered necessary to determine the effect of these separately and in combination on its oil and protein contents of the seed.

MATERIAL AND METHODS

A manurial trial was laid out with five levels of nitrogen, *i.e.* 0, 40, 80, 120 and 160 lbs. N and two levels, 0 and 40 lbs each of P_2O_5 and K_2O per acre. Nitrogen was applied in the form of sulphate of ammonia, phosphates as superphosphate and potassium as potassium sulphate. The system of lay out was randomised block design with four replications. Samples of rai R.T. 11 were collected at the time of harvest, cleaned of any foreign material and stored in air-tight bottles before analysis.

The oil content was determined in Soxhlet's apparatus using solvent oil as extracting agent. Protein content was estimated by determining the total nitrogen by modified kjeldahl's method and multiplying it by factor 6.25. The analytical data is given in the table :—

Table Showing Oil and Protein Contents as affected due to nitrogenous fertilizers with and without P and K fertilizers.

Treatments	Oil %	Protein %
N ₀ P ₀ K ₀ (Control)	33.23	5.37
N ₀ P ₄₀ K ₄₀	34.78	5.56
N ₄₀ P ₀ K ₀	32.47	5.75
N ₄₀ P ₄₀ K ₄₀	33.27	5.78
N ₈₀ P ₀ K ₀	32.36	5.78
N ₈₀ P ₄₀ K ₄₀	32.60	5.75
N ₁₂₀ P ₀ K ₀	32.92	5.79
N ₁₂₀ P ₄₀ K ₄₀	32.88	5.78
N ₁₆₀ P ₀ K ₀	32.32	6.01
N ₁₆₀ P ₄₀ K ₄₀	31.64	5.78
Correlation Factor Oil and Protein		
	$r = 0.54$	

DATA AND DISCUSSION

Oil Content :—Maximum oil content was obtained by the combined application of phosphates and potash, each at 40 lbs. per acre without nitrogen. Lowest oil content was observed where nitrogen at 160 lbs. per acre was applied with P₂ O₅ and K₂O each at 40 lbs. per acre. It may, however, be noted that the increasing doses of nitrogen singly or in conjunction with P₂ O₅ and K₂O showed a depressing effect on oil content. It may be presumed that phosphates and potash fertilizers favourably effect the oil content of *rai*.

Protein Content :—Highest protein content was observed where nitrogen was applied singly at 160 lbs. N per acre. In all other treatments except control the protein content is almost similar. Lowest protein content was observed in control samples where none of the fertilizers were applied.

Statistical analysis of the data indicated that oil and protein contents are negatively correlated.

SUMMARY

1. Oil content decreased with the increased nitrogenous fertilization where P and K fertilization responded favourably.
2. Correlation coefficient between oil and protein was inversely proportional.

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REFERENCES

1. Anderson, A., dsson, G and Loof, B., *Sv. Utsadesf Tidskrift*, 66, 39 (1956).
2. Bjorklund, C. M., and Wahlgreen, A., *Sv. Oljeaz Forsoksbohm Kristianstad* (1955).
3. Blackmann G. E. and Bunting, E.S., *Jour. Agric. Sci.* 41, 256 (1951).
4. Sen, P. D. and Sircar A. K., *Ind. Agric.*, 2, 113 (1958).
5. Sing, H Gupta M. L., and Auanta Rao, N. K., *Ind. Agron.*, 4, 176 (1950).
6. Sinha, N. S., M. Singh and Agrwal, P. N., *Jour. Oil Techn*, 16, 3 (1961).
7. Sinha, N. S., M. Singh and Agrwal P. N., *Ind. Oilseeds Jour.*, 6, 3 (1951).

ON SPATIAL GAS FLOWS

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ABSTRACT

If a relation like $f(p, q, s) = 0$ exists where ' p ' is the pressure, ' q ' the velocity and ' s ' the entropy of a gas, for any equation of state the four normals at a point to the surfaces of constant pressure, density, entropy, and velocity are coplanar. The results of Smith [1963] become a particular case of the foregoing.

§ 0 Introduction :—Smith [1963] has shown that the normals at a point to surfaces of constant pressure, density, entropy and velocity magnitude are coplanar, for the reduced velocity field of a steady gas flow, which is inviscid and non-conducting assuming the product equation of state. A similar result has been proved by Hassen and Martin [1] for plane flows. In this note, it has been demonstrated that the above four normal are coplanar considering the given flow itself instead of the reduced field, if there is a relation like $f(p, q, s) = 0$, for any general equation of state $F(p, q, s) = 0$. The converse is also true. All the results of Smith [2] follow at once.

§ 1. (A) Basic Equations :

The basic equations governing an inviscid, thermally non-conducting, steady gas flows in the absence of extraneous forces are given below :

$$\text{[Continuity]} \quad \nabla \cdot (\rho \vec{q}) = 0 \quad (1)$$

$$\text{[Momentum]} \quad \frac{1}{\rho} \nabla p + (\vec{q} \cdot \nabla) \vec{q} = 0$$

$$\text{or} \quad \frac{1}{\rho} \nabla p + \vec{\zeta} \wedge \vec{q} + \frac{1}{2} \nabla q^2 = 0 \quad (2)$$

$$\text{[Energy]} \quad \vec{q} \cdot \nabla S = 0 \quad (3)$$

$$\text{[State]} \quad \rho = \rho(p, S) \quad (4)$$

Using (2), (3) and (4) we have

$$q^2 + 2h(p, S) = 2h_0(p_0, S_0) = a^2 \quad (5)$$

where the enthalpy $h(p, S)$ is defined by

$$h(p, S) = \int_0^p \frac{dp}{\rho(p, S)} \quad (6)$$

and ' a^2 ' is constant along individual streamline.

(B) We shall prove that the normals to the surfaces

$[(p, q, S, \rho) = \text{constant}]$ are coplanar, if there exists a functional relation between p, q and S and the converse.

Let there exists a relation between p, q and S

$$f(p, q, S) = 0 \quad (7)$$

Also the equation of state can be written as

$$F(p, \rho, S) = 0 \quad (8)$$

Now operating ∇ on the above (7) and (8) we have

$$\nabla q = - \frac{1}{f_q} [f_p \nabla p + f_S \nabla S] \quad (9)$$

and

$$\nabla \rho = - \frac{1}{F_\rho} [F_p \nabla p + F_S \nabla S] \quad (10)$$

Taking the vector product of (9) and (10) we get

$$\nabla q \wedge \nabla \rho = \frac{1}{f_q F_\rho} \frac{\partial (f, F)}{\partial (p, S)} (\nabla p \wedge \nabla S)$$

forming the vector product of this by $\nabla p \wedge \nabla S$ we get

$$(\nabla q \wedge \nabla \rho) \wedge (\nabla p \wedge \nabla S) = 0 \quad (11)$$

which proves that the normals to the surfaces

$[(p, q, \rho, S) = \text{constant}]$ are coplanar.

This has been proved by Smith [2] for reduced flows, assuming the product equation of state.

It may be observed that the relation (7) is true in the case of homeenergetic flows, we have the following theorem :

1 Theorem : If there exist a functional relation between p, q and S , then the normals to the surfaces $[(p, q, \rho, S) = \text{constant}]$ are coplanar.

We now prove the converse theorem i.e. if the normals to the above surfaces are coplanar, then p , S and q must be functionally related.

If the normals are coplanar then (11) must hold good. Substituting for $\nabla \rho$ from (10) into (11) and after a little simplification we get

$$(\nabla q \wedge \nabla p) \cdot \nabla S F_p \nabla \rho = 0$$

Since $F_p \neq \nabla \rho \neq 0$, we should have

$$(\nabla q \wedge \nabla p) \cdot \nabla S = 0 \quad (12)$$

which shows that p , q and S are functionally related.

Hence the necessary and sufficient condition that the normals to the surfaces $[(p, \rho, q, S) = \text{constant}]$ should be coplanar is that there should exist a functional relation between p , q and S .

Following Smith [2] the cross-ratio ' λ ' formed by the above normals is

$$\lambda = \frac{(\nabla p \wedge \nabla S) \cdot (\nabla \rho \wedge \nabla q)}{(\nabla p \wedge \nabla q) \cdot (\nabla \rho \wedge \nabla S)} \quad (13)$$

Substituting for ∇q and $\nabla \rho$ from (9) and (10) in (13) we obtain

$$\lambda = 1 - \frac{F_S f_p}{F_R f_S} \quad (14)$$

From this it can be shown that the ' λ ' shall be constant along individual isobar, if the equation of state is of the form $\rho = P(p) S(s)$, further it shall be equal to γ the adiabatic exponent if $P(p) = p^{1/\gamma}$.

§2. We shall now assume the functional relation between p , q , S and a , where ' a ' is constant along individual streamline and investigate the condition that the normals to the surfaces $[p, q, \rho, S) = \text{constant}]$ should be coplanar.

Let the relation be

$$g(p, q, S, a) = 0 \quad (15)$$

operating ∇ on (15) we get

$$\nabla g = - \frac{1}{g_a} [g_p \nabla p + g_q \nabla q + g_S \nabla S + g_a \nabla a] \quad (16)$$

Substituting (16) in (11) we obtain

$$\frac{g_a}{g_q} \nabla \rho (\nabla a \wedge \nabla p) \cdot \nabla S = 0 \quad (17)$$

From this we have either

$$(\alpha) (\nabla a \wedge \nabla p) \cdot \nabla S = 0 \text{ or } (\beta) g_a = 0 \text{ since } \nabla p \neq 0$$

The condition ' β ' reduces to the above relation (7)

The condition ' α ' simplifies to either

$$p_s = 0 \text{ or } S = S(a)$$

In the first case all the surfaces coincide [3]. Therefore the relation (15) reduces to $g\{p, q, S(a)\} = 0$.

This is true for iso-energetic flows, in which the stagnation enthalpy is constant along individual streamlines.

REFERENCES

1. Hassen, A. G. and Martin, M.H., *Proc. Camb. Phil. Soc.*, 47, 763 (1951).
2. Smith P. : *J. Maths. and Mech.*, 12, 27 (1963).
3. Venugopala Cahri, R. and Purushotham, G., Communicated to the *Proc. Nat. Acad. Sci., India*.

ON SOME IDENTITIES IN THEORY OF PARTITION

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ABSTRACT

The Rogers—Ramanujan identities are

$$1 - \sum_{n=1}^{\infty} \frac{x^{n^2}}{(1-x)(1-x^2)\dots(1-x^n)} = \prod_{n=0}^{\infty} \frac{1}{(1-x^{5n+1})(1-x^{5n+4})}$$

and $1 + \sum_{n=1}^{\infty} \frac{x^{n(n+1)}}{(1-x)(1-x^2)\dots(1-x^n)} = \prod_{n=0}^{\infty} \frac{1}{(1-x^{5n+2})(1-x^{5n+3})}$

Here the following new identities are found :—

$$\prod_{n=0}^{\infty} \frac{1}{(1-x^{7n+2})(1-x^{7n+3})(1-x^{7n+4})(1-x^{7n+5})} = \frac{1-x-x^6(1-x^3)+x^{10}(1-x^3)}{\prod_{n=1}^{\infty} (1-x^n)} \quad (1)$$

$$\prod_{n=0}^{\infty} \frac{1}{(1-x^{7n+1})(1-x^{7n+3})(1-x^{7n+4})(1-x^{7n+6})} = \frac{1-x^2-x^5(1-x^3)+x^{17}(1-x^{10})}{\prod_{n=1}^{\infty} (1-x^n)} \quad (2)$$

$$\prod_{n=0}^{\infty} \frac{1}{(1-x^{7n+1})(1-x^{7n+2})(1-x^{7n+5})(1-x^{7n+6})}$$

$$= \frac{1-x^3-x^4(1-x^3) + x^{15}(1-x^{15})}{\prod_{n=1}^{\infty} (1-x^n)} \quad \dots (3)$$

$$p_7(n) = p(n) - p(n-2) - p(n-5) + p(n-11) + p(n-17) \quad \dots (4)$$

$$p_7'(n) = p(n) - p(n-1) - p(n-6) + p(n-9) + p(n-19) \quad \dots (5)$$

$$p_7''(n) = p(n) - p(n-3) - p(n-4) + p(n-13) + p(n-15) \quad \dots (6)$$

Where $p_7(n)$ denotes the number of partitions of n into parts of the forms $7n+1$, $7n+3$, $7n+4$, $7n+6$.

$p_7'(n)$ = the number of partitions of n into parts of the forms $7n + 2, 7n + 3, 7n + 4, 7n + 5$.

$p_7''(n)$ = the number of partitions of n into parts of the forms $7n + 1, 7n + 2, 7n + 5, 7n + 6$

The Rogers - Ramanujam identities (1) are

$$1 + \sum_{m=1}^{\infty} \frac{x^{m^2}}{(1-x)(1-x^2)\dots(1-x^m)} = \frac{1}{\prod_{m=0}^{\infty} (1-x^{5m+1})(1-x^{5m+4})}$$

$$\text{and } 1 + \sum_{m=1}^{\infty} \frac{x^{m(m+1)}}{(1-x)(1-x^2)\dots(1-x^m)} = \frac{1}{\prod_{m=0}^{\infty} (1-x^{5m+2})(1-x^{5m+3})}$$

Here I shall consider similar new identities.

We know the Jacobi's identity (2)

$$\prod_{n=0}^{\infty} (1-x^{2kn+k-l})(1-x^{2kn+k+l})(1-x^{2kn+2k}) = \sum_{n=-\infty}^{\infty} (-1)^n x^{kn^2+ln}$$

$$\text{Putting } k = \frac{7}{2}, l = \frac{5}{2}; k = \frac{7}{2}, l = \frac{3}{2}; k = \frac{7}{2}, l = \frac{1}{2}$$

We have the following identities :

$$\prod_{n=0}^{\infty} (1-x^{7n+1})(1-x^{7n+4})(1-x^{7n+7}) = \sum_{n=-\infty}^{\infty} (-1)^n x^{\frac{n(7n+5)}{2}} = 1 + \sum_{n=1}^{\infty} (-1)^n \left[x^{\frac{n(7n+5)}{2}} + x^{\frac{n(7n-5)}{2}} \right]$$

$$= 1 - x - x^6(1-x^3) + x^{10}(1-x^5) - x^{39}(1-x^7) + \dots \quad (1)$$

$$\prod_{n=0}^{\infty} (1-x^{7n+2})(1-x^{7n+5})(1-x^{7n+7}) = 1 + \sum_{n=1}^{\infty} (-1)^n \left[x^{\frac{n(7n+3)}{2}} + x^{\frac{n(7n-3)}{2}} \right]$$

$$= 1 - x^2 - x^5(1-x^3) + x^{17}(1-x^{10}) - x^{36}(1-x^{14}) + \dots \quad (2)$$

$$\begin{aligned}
& \prod_{n=0}^{\infty} (1-x^{7n+3})(1-x^{7n+4})(1-x^{7n+7}) \\
&= 1 + \sum_1^{\infty} \left[(-1)^n \left\{ x^{\frac{n(7n+1)}{2}} + x^{\frac{n(7n-1)}{2}} \right\} \right] \\
&= 1-x^3-x^4(1-x^7)+x^{13}(1-x^{15})-\dots \dots \dots (3)
\end{aligned}$$

$$\begin{aligned}
\text{Then } & \prod_{n=0}^{\infty} \frac{1}{(1-x^{7n+2})(1-x^{7n+3})(1-x^{7n+4})(1-x^{7n+5})} \\
&= \frac{1-x-x^6(1-x^8)+x^{19}(1-x^5)}{\prod_{n=1}^{\infty} (1-x^n)} \dots \dots \dots (4)
\end{aligned}$$

$$\begin{aligned}
& \prod_{n=0}^{\infty} \frac{1}{(1-x^{7n+1})(1-x^{7n+3})(1-x^{7n+4})(1-x^{7n+6})} \\
&= \frac{1-x^2-x^5(1-x^8)+x^{17}(1-x^{10})}{\prod_{n=0}^{\infty} (1-x^n)} \dots \dots \dots (5)
\end{aligned}$$

$$\begin{aligned}
& \prod_{n=0}^{\infty} \frac{1}{(1-x^{7n+1})(1-x^{7n+2})(1-x^{7n+5})(1-x^{7n+6})} \\
&= \frac{1-x^2-x^4(1-x^9)+x^{15}(1-x^{15})}{\prod_{n=1}^{\infty} (1-x^n)} \dots \dots \dots (6)
\end{aligned}$$

Let $p_7(n)$ = the number of partition of n into parts of the forms : $7n+1, 7n+3, 7n+4, 7n+6$.

$p_7'(n)$ = the number of partition of n into parts of the forms : $7n+2, 7n+3, 7n+5$.

$p_7''(n)$ = the number of partition of n into parts of the forms : $7n+1, 7n+2, 7n+5, 7n+6$.

and $p(n)$ = the number of partition of n .

$$\text{Then we have } \sum_0^{\infty} p_7(n)x^n = (1-x^2-x^5+x^{11}+x^{17}-\dots) \sum_0^{\infty} p'(n)x^n \text{ by (5)} \quad (7)$$

$$\text{Hence } p_7(n) = p(n) - p(n-2) - p(n-5) + p(n-11) + p(n-17)$$

$$\text{Similarly } p_7'(n) = p(n) - p(n-1) - p(n-6) + p(n-9) + p(n-19) \quad \text{by (4)} \dots (8)$$

Similarly $p_r''(n) = p(n) - p(n-3) - p(n-4) + p(n-13) + p(n-15)$ by (6) ... (9)

$$\text{Let } G_m(a, x) = \sum_{r=0}^{\alpha} (-1)^r a^{3r} x^{\frac{r}{2}(7r+1) - mr} (1 - a^{2m} x^{2mr}) C_r$$

$$\text{Where } C_r = \frac{(1-a)(1-ax) \dots (1-ax^{r-1})}{(1-x)(1-x^2) \dots (1-x^r)} \quad (7 > 0)$$

Then $C_r = 1$ if $a = x$

$$G_1(x, x) = 1 - x - x^3(1-x^3) + x^{10}(1-x^5)$$

$$G_2(x, x) = 1 - x^2 - x^5(1-x^3) + x^{17}(1-x^{10})$$

$$G_3(x, x) = 1 - x^3 - x^4(1-x^3) + x^{15}(1-x^{15})$$

$$\text{Let } \eta f(a, x) = f(ax, x)$$

$$\text{Then } \eta C_r = \frac{1-ax^r}{1-a} C_r, \quad \eta C_{r-1} = \frac{1-x^r}{1-a} C_r \dots \quad \dots (10)$$

$$G_m - G_{m-1} = \sum_{r=0}^{\alpha} (-1)^r a^{3r} x^{\frac{r}{2}(7r+1) - mr} (1 - a^{2m} x^{2mr}) C_r$$

$$= \sum_{r=0}^{\alpha} (-1)^r a^{3r} x^{\frac{r}{2}(7r+1) - (m-1)r} (1 - a^{m-1} x^{2r(m-1)}) C_r$$

$$= \sum_{r=0}^{\alpha} (-1)^r a^{3r} x^{\frac{r}{2}(7r+1) - mr} [1 - a^{m-1} x^{2rm} - x^r(1 - a^{m-1} x^{2r(m-1)})] C_r$$

$$= a^{m-1}(1-a) + \sum_{r=1}^{\alpha} (-1)^r a^{3r} x^{\frac{r}{2}(7r+1) - mr} [1 - x^r + a^{m-1} x^{(2m-1)r}] \times$$

$$(1 - ax^r) C_r = a^{m-1}(1-a) \eta C_0 + (1-a) \sum_{r=1}^{\alpha} (-1)^r a^{3r} x^{\frac{r}{2}(7r+1) - mr}$$

$$[\eta C_{r-1} + a^{m-1} x^{(2m-1)r} \eta C_r] \text{ by (10)}$$

The Coefficient of ηC_r is

$$(-1)^r a^{3r} x^{\frac{r}{2}(7r+1) - mr} a^{m-1} x^{(2m-1)r}$$

$$-a^{3r+3} x^{\frac{(r+1)}{2} (7r+8) - m(r+1)} (-1)^r$$

$$= (-1)^r a^{3r+m-1} x^{\frac{r}{2} (7r+1) + (m-1)r} [1 - a^{4-m} x^{(4-m)(2r+1)}]$$

$$\text{Hence } G_m - G_{m-1} = a^{m-1} (1-a) \sum_0^{\alpha} (-1)^r a^{3r} \times$$

$$x^{\frac{r}{2} (7r+1) + (m-1)r} [1 - a^{4-m} x^{(4-m)(2r+1)}]$$

$$G_{4-m} = \sum_0^{\alpha} (-1)^r a^{3r} x^{\frac{r}{2} (7r+1) + (m-1)r} \times$$

$$[1 - a^{4-m} x^{(4-m)(2r+1)}] G_r$$

$$\eta G_{4-m} = \sum_0^{\alpha} (-1)^r a^{3r} x^{\frac{r}{2} (7r+1) + (m-1)r} [1 - a^{4-m} x^{(4-m)(2r+1)}] \eta G_r$$

$$\text{Hence } G_m - G_{m-1} = a^{m-1} (1-a) \eta G_{4-m}$$

$$\text{Let } H_m(ax) = \frac{G_m(a, x)}{(1-a)(1-ax) \dots (1-ax^r) \dots}$$

$$\mu H_m(a, x) = \frac{\eta G_m(a, x)}{(1-ax)(1-ax^r) \dots}$$

$$\text{Hence } H_m - H_{m-1} = a^{m-1} \eta H_{4-m}$$

$$\text{If } H_0 = 0 \text{ Then } H_1 = \eta H_2, H_2 - H_1 = a\eta H_2$$

$$\text{and } H_3 - H_2 = a^2 \eta H_1$$

$$\text{Hence } H_1 = \eta H_3 = \eta a H_1 + \eta a^3 \eta H_1 = \eta a \eta a^2 \eta H_1 + \eta H_1$$

$$\text{Let } H_1 = 1 + c_1 a + c_2 a^2 + c_3 a^3 + \dots \dots C_r a^r + \dots \dots$$

$$\text{Then } c_1 = \frac{x}{1-x}, c_2 = \frac{x^2}{(1-x)(1-x^2)} = \frac{x}{1-x^2} C_1$$

$$c_3 = c_2 \frac{x^3}{1+x^2} + c_1 \frac{x^4}{1-x^3} = \frac{x^5}{1-x^3} \text{ and}$$

$$C_r = C_{r-1} \frac{x^r}{1-x^r} + C_{r-2} \frac{x^{2r-2}}{1-x^r} C_{r-3} \frac{x^{5r-4}}{1-x^r} \quad (r > 3) \dots (11)$$

Putting $r-1, r-2, \dots 4$ for x in (11) and eliminating $C_{r-1}, C_{r-2}, \dots c_1$ we have

$$\begin{vmatrix} -C_r & \frac{x^r}{1-x^r} & \frac{x^{2r-2}}{1-x^r} & \frac{x^{3r-4}}{1-x^r} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & \frac{x^{r-1}}{1-x^{r-1}} & \frac{x^{2r-3}}{1-x^{r-1}} & \frac{x^{3r-5}}{1-x^{r-1}} & 0 & 0 & 0 & 0 & 0 \\ & & -\frac{x^5}{1-x^3} & -1 & -\frac{x^7}{1-x^3} & \frac{x^4}{1-x^3} & & & & \\ & & & & 0 & -1 & \frac{x}{1-x^2} & & & \\ & & & & & & \frac{x}{1-x} & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{vmatrix} = 0$$

From this determinantal equation we get the value of C_r .

It is evident that $L_t C_r \dots 0$ if $|x| < 1$

$$r = \alpha$$

Hence $H_1(a, x)$ is convergent if $|x| < 1$ and $|a| < 1$

Let $H_3 = 1 + c_1^1 a + c_2^1 a^2 + \dots + c_r^1 a^r +$

Then since $H_1 = \eta H_3$ we have $C_r = c_r^1 x^r$

Similarly if $H_2 = 1 + c_1'' a + c_2'' a^2 + \dots + c_r'' a^2 +$

We have $C_r'' = C_r^1 C_{r-2} x^{r-2}$

$$H_1(a, x) = \frac{G_1(a, x)}{(1-a)(1-ax)(1-ax^2)} \dots \dots \dots (12)$$

$$H_1(x, x) = \frac{G_1(x, x)}{(1-x)(1-x^2)} \dots \dots \dots (13)$$

$$H_2(a, x) = \frac{G_2(a, x)}{(1-a)(1-ax)(1-ax^2)} \dots \dots \dots (14)$$

$$H_2(x, x) = \frac{G_2(x, x)}{(1-x)(1-x^2)} \dots \dots \dots (15)$$

$$H_3(a, x) = \frac{G_3(a, x)}{(1-a)(1-ax)(1-ax^2)} \dots \dots \dots (16)$$

$$H_3(x, x) = \frac{G_3(x, x)}{(1-x)(1-x^2)} \dots \dots \dots (17)$$

REFERENCES

1. Hardy, G. H. and Wright, E. M., An introduction to the theory of numbers (Third edition) p. 290.
2. Hardy, G. H. and Wright, E. M., I.C. p. 282.

FINITE SIMPLE TENSION

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ABSTRACT

The object of the paper is to consider the problem of simple tension of an isotropic rod, using non linear components of strain, and a non-linear stress-strain relation. A parabolic tension stretch curve is obtained, which is used in obtaining the stretched lengths of suspended strings when either a weight is attached to the free end or when the string stretches by its own weight. Youngs' moduli in both cases are calculated.

We consider an isotropic rod of uniform cross-section with both ends subjected to a uniformly distributed tension T , the curved surface being stress-free.

The following non-linear components of strain and stress-strain relations are used with the usual notation :

$$2 \epsilon_{ij} = u_{i,j} + u_{j,i} - u_{k,i} u_{k,j}$$

$$T_{ij} = \lambda I_1 (1 - I_1) \delta_{ij} + 2 [\mu - (\lambda + \mu) I_1] \epsilon_{ij} - 4\mu \epsilon_{\alpha i} \epsilon_{\alpha j}$$

Using a rectangular cartesian reference frame, the displacement components u, v, w are assumed as follows :

$$u = x(1 - p); v = y(1 - q); w = z(1 - r)$$

(1.1) where p, q, r are constants.

The components of strain are

$$\epsilon_{xx} = \frac{1}{2}(1 - p^2); \epsilon_{yy} = \frac{1}{2}(1 - q^2); \epsilon_{zz} = \frac{1}{2}(1 - r^2)$$

$$\epsilon_{yz} = \epsilon_{zx} = \epsilon_{xy} = 0$$

(1.2) Obviously the body-stress equations of equilibrium are identically satisfied.

Now the following stress-strain relations are used.

$$T_{xx} = \lambda I_1 (1 - I_1) + 2 [\mu - (\lambda + \mu) I_1] \epsilon_{xx} - 4\mu [\epsilon_{xx}^2 + \epsilon_{yy}^2 + \epsilon_{zz}^2]$$

$$T_{xy} = 2 [\mu - (\lambda + \mu) I_1] \epsilon_{xy} - 4\mu [\epsilon_{xx}\epsilon_{xy} + \epsilon_{xy}\epsilon_{yy} + \epsilon_{xz}\epsilon_{yz}]$$

The boundary conditions $T_{xx} = T_{yy} = T_{xy} = T_{yz} = T_{zx} = 0$

and $T_{zz} = T$ yield

$$\begin{aligned} \lambda [3/2 - \frac{1}{2}(p^2 + q^2 + r^2)] - \lambda [9/4 + \frac{1}{4}(p^2 + q^2 + r^2)^2 - 3/2(p^2 + q^2 + r^2)] \\ + \mu(1 - p^2) - (\lambda + \mu) [3/2 - \frac{1}{2}(p^2 + q^2 + r^2)](1 - p^2) \\ - \mu(1 - p^2)^2 = 0 \end{aligned}$$

(1.3) and

$$\begin{aligned} & \mu [3/2 - \frac{1}{2} (p^2 + q^2 + r^2)] - \lambda [9/4 + \frac{1}{4} (p^2 + q^2 + r^2)^2 - 3/2 (p^2 + q^2 + r^2)] \\ & + \mu (1 - q^2) - (\lambda + \mu) [3/2 - \frac{1}{2} (p^2 + q^2 + r^2)] (1 - q^2) \\ & - \mu (1 - q^2)^2 = 0 \end{aligned}$$

and

$$\begin{aligned} & \lambda [3/2 - \frac{1}{2} (p^2 + q^2 + r^2)] - \lambda [9/4 + \frac{1}{4} (p^2 + q^2 + r^2)^2 - 3/2 (p^2 + q^2 + r^2)] \\ & + \mu (1 - r^2) - (\lambda + \mu) [3/2 - \frac{1}{2} (p^2 + q^2 + r^2)] (1 - r^2) \\ & - \mu (1 - r^2)^2 = T \end{aligned}$$

These immediately give $p^2 = q^2$ and

$$\begin{aligned} (1.4) \quad & (\lambda + \mu) (r^2 - p^2) [3/2 - \frac{1}{2} (2p^2 + r^2)] - \mu (r^2 - p^2) \\ & + \mu (r^2 + p^2) (2 - r^2 - p^2) - T = 0 \end{aligned}$$

The poisson's ratio $\sigma = -\frac{6_{xx}}{6_{zz}} = -\frac{6_{yy}}{6_{zz}}$ gives

(1.5) $r^2 = \frac{1}{\sigma} (1 + \sigma - p^2)$, so that we have a single biquadratic equation in p , given by

$$(1.6) \quad p^4 - \frac{5\lambda + 6\mu}{2\lambda + 3\mu} p^2 + \frac{3\mu(\lambda + \mu)(3\lambda + 2\mu) + \lambda T^2}{\mu(2\lambda + 3\mu)(3\lambda + 2\mu)} = 0$$

Regarded as a quadratic equation in p^2 , both the roots are obviously seen to be positive.

The condition for real roots of p^2 is

$$(1.7) \quad T \leq \frac{\mu(3\lambda + 2\mu)}{4(2\mu + 3\mu)}$$

which qualitatively suggests the yield stress

$$(1.8) \quad T = \frac{E}{4(3 - 2\sigma)}$$

This yield stress is much higher than the one got experimentally. The Youngs' modulus 'E' should be replaced by the 'modified Youngs' modulus E_0 , because near the break-point strain increases much more rapidly than stress and the ordinary Hooke's law $T = ES$ does not hold, but rather the relation $T = E_0 S$ holds, where E_0 is much smaller than the actual E, to be adjusted from experimental data.

Writing 'S' for the ordinary stretch the tension-stretch curve turns out to be given by :—

$$(1.9) \quad T = \frac{\mu(3\lambda + 2\mu)}{2\lambda + 3\mu} - \frac{\mu(2\lambda + 3\mu)(3\lambda + 2\mu)}{(\lambda + \mu)^2} \left\{ \frac{1}{(1 + S)^2} - \frac{\lambda + 2\mu}{2\lambda + 3\mu} \right\}^2$$

This in turn reduces to

$$(1.10) \quad T = 16 E \sigma \left(S - \frac{1+4\sigma}{2\sigma} S^2 + \text{higher terms in 'S'} \right)$$

which is in agreement with Gerstner's empirical formula

$$T = AS - BS^2$$

From (1.5) and (1.6) it is seen that both values of r^2 corresponding to the two positive value of p^2 are also real and positive. Thus we get two distinct solutions of the tension problem, corresponding to the same load. These two solutions correspond to the stretches which are got for the load T when first the string is subjected to increasing loads, and secondly when the experiment is repeated with the loads gradually decreased. And experimentally it is known that the material exhibits a kind of 'hysteresis' when subjected to the above treatment. For less precise experiments the lesser of the two values should be taken, as it corresponds to the state which is realised first.

It is proposed to apply the results in (1.9) to two simple cases, when

- (1) An elastic string is suspended by one end and a weight is attached to the other end, and (2) An elastic string, suspended by one end, is stretched by its own weight.

Let the initial length be l_1 and the extended length l . If dx and dx_1 are the line elements in the deformed and undeformed states, the extension 'S' is given by

$$(1.2) \quad S = \frac{dx - dx_1}{dx_1}$$

Also, if ω is the weight per unit length of the unstretched string and W is the weight attached to the free end, the tension T , at a point lying at a distance x_1 , from the point of suspension in the initial state, is given by

$$(1.3) \quad T = \omega (l_1 - x_1) + W$$

From (1.1), (1.2) and (1.3) we get

$$(1.4) \quad \left[\left(\frac{dx_1}{dx} \right)^2 - \frac{\lambda + 2\mu}{2\lambda + 3\mu} \right]^2 = \left(\frac{\lambda + \mu}{2\lambda + 3\mu} \right)^2 \left[1 - \frac{2\lambda + 3\mu}{(\lambda + \mu)E} \left\{ \omega (l_1 - x_1) + W \right\} \right]$$

It is evident from (1.4) that $\frac{2\lambda + 3\mu}{(\lambda + \mu)E} \left\{ \omega (l_1 - x_1) + W \right\} < 1$

Therefore we can write approximately

$$(1.5) \quad \left(\frac{dx_1}{dx} \right)^2 = 1 - \frac{1}{2E} \left\{ \omega (l_1 - x_1) + W \right\} \quad \text{giving}$$

$$(1.6) \quad x = \frac{4E}{\omega} \left[\left\{ 1 - \frac{1}{2E} \left(\omega (l_1 - x_1) + W \right) \right\}^{1/2} - \left\{ 1 - \frac{1}{2E} (\omega l_1 + W) \right\}^{1/2} \right]$$

Therefore the extended length is

$$(1.7) \quad l = \frac{4E}{\omega} \left[\left\{ 1 - \frac{W}{2E} \right\}^{1/2} - \left\{ 1 - \frac{1}{2E} (\omega l_1 + W) \right\}^{1/2} \right]$$

If $W = 0$

$$(1.8) \quad l = \frac{4E}{\omega} \left[1 - \left(1 - \frac{\omega l_1}{2E} \right)^{1/2} \right] \quad \text{giving}$$

$$(1.9) \quad E = \frac{l_1^2 \omega}{8(l - l_1)}$$

If the weight of the string is negligible compared to the weight attached at its free end the extended length is

$$(1.10) \quad l = \left(1 - \frac{W}{2E} \right)^{-1/2} l_1 \quad \text{giving}$$

$$(1.11) \quad E = \frac{\omega l_1^2}{2(l^2 - l_1^2)}$$

REFERENCES

1. Seth, B. R., Finite Strain in Elastic Problems, *Philos. Trans. Roy. Soc. London*, 234 (1935).
2. Seth, B. R., Some problems of finite strain, *Phil. Mag.*, 27 (1939).
3. Seth B. R., On Young's modulus for India Rubber, *Bull. Cal. Math. Soc.*, 38, 143 (1946).
4. Seth, B. R., An application of the theory of finite strain, *Proc. Ind. Acad. Sci.*, 9A (1939).

STABILITY OF LYOPHOBIC COLLOIDS—PART III
PHYSICO-CHEMICAL PROPERTIES OF THE SOLS OF HYDROUS
FERRIC OXIDE AS OBTAINED BY VARIOUS METHODS OF
THE PREPARATION WITH REFERENCE TO THEIR
STABILITY RELATION

By

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ABSTRACT

Stability of the colloidal solutions are highly dependent on the mode of their preparation such that their behaviour towards an electrolyte, employed for coagulation show much variation. For the present study sols of hydrous ferric oxide were prepared both positively and negatively charged by six different methods and three samples of the sols were obtained containing varying amounts of the free peptising agents by each method. Coagulation studies were performed by noting the time of complete coagulation towards their precipitation with potassium chloride, sulphate, ferricyanide (for positively charged sols) and potassium chloride, barium chloride, aluminium chloride (for negatively charged sols). Precipitation values were expressed in terms of activities and it was found that the stability of these sols towards their coagulation in infinite time, though containing same amount of iron and pH., differed widely depending upon the structure of the dispersed colloidal units and their free surface energy.

As reported earlier⁹, the sols of hydrous ferric oxide can be prepared of varying properties by different methods and it is of interest to investigate the variation of the properties of the different sols containing the same amount of iron and of the same pH., value. The investigation described in this paper deals with a comparative study of eighteen different positively and negatively charged sols of hydrous ferric oxide obtained by six different methods.

Following are the details of the preparation of the positively charged hydrous ferric oxide sols :

- (a) *Krecke's method*⁶. A fairly concentrated aqueous solution of ferric chloride (B.D.H.) was added drop by drop (at the rate of two drops per minute) from a burette to boiling distilled water taken in a jena flask. A clear deep wine red coloured sol was obtained which was dialysed in a cellophane bag, in a running current of hot distilled water. The dialysis was continued to different extents, so as to obtain sols of varying pH.
- (b) *Graham's Method*⁸ : Ammonium hydroxide was slowly added to a concentrated solution of ferric chloride with constant stirring. The addition of ammonium hydroxide was continued till further addition of ammonia produced a precipitate which could not be peptised by shaking. The precipitate so obtained was washed by decantation, till the precipitate got partially peptised. The precipitate was now mixed with few ml., of 2N hydrochloric acid (as suggested by Müller⁸) and shaken with a microid shaker. A brick red sol was obtained and this mother sol was

dialysed to different extents as already described, to obtain three samples of the sols of varying pH.

- (c) *Pean De St. Gilles Method*¹¹: This method was modified. Instead of heating a solution of ferric acetate on water bath for several days, the hydrous oxide (obtained as described in the previous case) was mixed with few ml., of glacial acetic acid and a sol was obtained by shaking (as described for the sol prepared by Graham's Method) which was deep brick red in colour and appeared turbid in reflected light, but was clear in transmitted light,

Preparation of the negatively charged hydrous ferric oxide sols :

As early as 1823 Rose¹², observed that the presence of glycerol, mannitol, sucrose and glucose prevent the precipitation of hydrous ferric oxide on adding alkali or ammonia to a solution of ferric salt. This observation was attributed by Grimaux⁴ to the formation of a red negative sol stabilized by preferential adsorption of the hydroxyl ion⁴. For the present study, negatively charged sols have been obtained by peptising the hydrous oxide with sodium hydroxide in the presence of either arsenious oxide or glucose or glycerol. Slightly modified methods were, however, employed so as to prepare stable sols with a greater ease and these are described below :—

5 mls., of a standard 4N sodium hydroxide (E. Merck) were taken in a jena flask of one litre capacity. 250 mls., of aqueous arsenic oxide (B. D. H.) solution N/2.4311) were added to it. The contents were made to 200 mls. with distilled water. The flask was now shaken at a low speed by a macroid shaker and arrangements were made to add drop by drop a strong solution (1.56N) of ferric chloride (B.D.H.) at intervals of two minutes from a microburette. After adding 2 ml., of ferric chloride, the volume was finally raised upto 500 ml., with distilled water. Thus, a pale opaque red, negatively charged, hydrous ferric oxide sol was obtained. However, attempts to prepare one litre of sol at a time yielded a comparatively unstable sol, because of less efficient shaking. By changing the alkali and arsenite concentrations sols of varying pH., and the stabilising agent arsenite, could be obtained. By similar treatments, samples of the sols having different pH., were prepared separately, stabilised by glucose or glycerol. (B.D.H. AnalaR samples). It was noted that the sols stabilised by glucose showed a drop in its pH., value with time but it became steady after 72 hours of the preparation of the sol. However, these negative sols were not subjected to dialysis, as it was found that some of the stabilising agents passed out through the cellophane bag, which markedly affect the stability of the prepared sols.

The iron contents of the positively charged sols were estimated volumetrically¹³, and the sols were so diluted as to have the same iron content. For the negatively charged sols, which were not dialysed, the amount of iron was calculated from the amounts of ferric chloride used in the preparation of sols. The chloride contents of all positively charged sols were also estimated volumetrically¹⁴ and the purity of the sol was designated by the ratio of the ferric to chloride present in a particular sol.

Samples of the various sols, thus prepared were nomenclatured as given in the table 1 (a and b) where suffix 1, 2, and 3 refer to the sols containing different amounts of the peptising agents.

TABLE 1 (a)

Compositions of the Positive Sols.

Iron content of the sol = 5.6296 gm/litre Fe^{+3} in each case

Method of preparation of the sol	Sol sample (symbol used)	pH of the sol	Chloride content of the sol (gm/litre)	Purity of the sol
Graham's	A ₁	2.2	0.96424	3.7642
Method	A ₂	3.6	0.31196	11.6348
	A ₃	4.5	0.18434	19.6897
Pean de st.	B ₁	2.9*	—	—
Gilles	B ₂	3.6	—	—
Method	B ₃	4.5	—	—
Krecke's	C ₁	2.2	0.6481	5.6003
Method	C ₂	3.6	0.2127	17.0644
	C ₃	4.5	0.10635	34.1288

TABLE 1 (b)

Compositions of the Negative Sols

Iron content of the sols = 0.6098 gm Fe^{+3} /litre

Chloride content of the sols = 1.5508 gm/litre

Total volume = 1 litre

Samples	Amount of stabilising agent employed	Amount of ferric chloride added	Amount of sodium hydroxide added	pH. the sol
(a) Sols stabilised by arsenious oxide.	35 ml. of N/2.4311 solution	7 ml. of 1.56N solution	18.33 ml. of 4N solution	12.15
(X ₁)	(1.0796 gm. of As^{+3} per litre)			

* This sol could not be obtained of lower pH value.

TABLE 1 (b).—(Contd.)

Samples	Amount of stabilising agent employed	Amount of ferric chloride added	Amount of sodium hydroxide added	pH. the sol
(X ₂)	95 ml. of N/2.4311 solution (2.9305 gm. of As ⁺³ per litre)	7 ml. of 1.56 N solution	17.33 ml. of 4N solution	10.80
(X ₅)	275 ml. of N/2.4311 solution (8.4831 gm. of As ⁺³ per litre)	„	15 ml. of 4N solution	7.80
(b) Sols stabilised by glucose (Y ₁)	10 ml. of M solution	„	15 ml. of 4N solution	8.75
(Y ₂)	25 ml. of M solution	„	15.54 ml. of 4N solution	10.30
(Y ₃)	35 ml. of M solution	„	19.29 ml. of 4N solution	11.25
(c) Sols stabilised by glycerol (Z ₁)	20 ml. of 13.6M solution	„	9.25 ml. of 4N solution	9.75
(Z ₂)	40 ml. of 13.6M solution	„	11.0 ml. of 4N solution	10.71
(Z ₃)	60 ml. of 16.6M solution	„	22.5 ml. of 4N solution	12.12

EXPERIMENTAL PROCEDURE EMPLOYED IN THE COAGULATION STUDIES OF THE SOLS OF HYDROUS FERRIC OXIDE

An estimate of the stability of a sol can be made by the study of its coagulation by an electrolyte. This has been studied by various methods *viz.*, ultramicroscopic counting of the particles,^{6,8,10} spectrophotometry¹⁰, Opacitometry², Turbidimetry³, Nephelometry etc. Such methods are based on the changes in the optical properties of the sols, during coagulation.

In the present study which involves a comparative assessment of the stability of hydrous ferric oxide, dispersed in water, optical methods were not followed. In fact, the optical property of a hydrous ferric oxide sol is greatly modified by the method of the preparation. Moreover, the original colour of the sol undergoes different changes for different sols during coagulation. Thus, positive sol prepared by Krecke's method during its coagulation by an electrolyte became deeper red and then turbid before a precipitate separated out, whilst, the sol peptised by acetic acid did not become equally turbid, even when a precipitate separated out in deep red flocks producing a bulky coagulum. The negative sols stabilised by arsenic oxide tend to appear as canary yellowish red and it becomes much turbid and the sol acquires a pale red tinge before it coagulates. Again, the sol stabilised by glucose, is deep red and stabilised by glycerol is orange deep red. According to Weiser,¹⁵ during the coagulation of clear red Graham sol, the absorption limit moves towards the red and finally turns to the violet region at complete coagulation. In general, the sols of hydrous ferric oxide varies in colour and these may be yellow, brown red, clear red and even cloudy brick coloured, depending on the various factors, besides the size of the particles. Pure α or β ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) yields red or yellow sols and those intermediate in colour between red and yellow may be the mixtures of hydrous oxide in different proportions. Hence, the optical methods for the study of coagulation of a hydrous ferric oxide sol cannot be dependable. Determination of coagulation value of an electrolyte for a definite time has also been frequently used for studying the stability, but it is well-known that the amount of an electrolyte required to coagulate a given sol depends on the time allowed for the observations. Here, we have determined the time of complete coagulation for different concentrations of the precipitating electrolyte and have evaluated the precipitation value for infinite time. Thus, the factor of time has been eliminated where, the slow coagulation is at its maximum. From these data, one can also evaluate the values for the rapid coagulation.

The Precipitating values of the Electrolytes. For determining the precipitating values of the electrolytes, 2 mls., of the sol were taken in each set of clean and dry test tubes. Different amounts of coagulating electrolytes were made upto 13 ml., with distilled water and were taken in another set. The test tubes chosen for the experiments were of the same size. Now these were kept in a precision thermostat,

till they attained the temperature of the bath. Such three similar sets of the tubes having same amounts of electrolyte were taken each time. The electrolyte was poured in the sol and the mixture was poured back in the emptied test tube immediately. The process was repeated and the test tube containing the sol and electrolyte was then left undisturbed in the thermostat. The coagulation was observed by the visual separation of the clear liquid at the upper layer of the sol electrolyte mixtures. The mean of the time of coagulation noted for each of the three tubes with the same amount of sol and the electrolyte was recorded. The results obtained were reproducible within the limits of experimental errors of $\pm 3\%$. It should however, be clearly stated here that the way, how the sol and the electrolyte were mixed and the way of noting the visual separation of the clear liquid in the tube, affect the time of observation. Hence, the details given above were strictly followed for the reproducibility of the results. Thus, the time of complete coagulation for a fixed amount of the sol (2 ml.) has been determined by different amounts of potassium chloride, potassium sulphate and potassium ferricyanide for the positively charged sols, whilst, for the negative ones, potassium chloride, barium chloride and aluminium chloride have been employed as a coagulating electrolyte. In the subsequent tables the precipitation values expressed in the terms of the activity of the different ions for infinite time, evaluated from results are only given.

*Precipitation values in terms of Active Mass of the Coagulating for Infinite time
of Coagulation*

TABLE 2
Positive Sols

Sol sample	Precipitation values for anions :—		
	Chloride	Sulphate $\times 10^3$	Ferricyanide $\times 10^5$
A ₁	0.0600	1.0000	0.9880
A ₂	0.0380	0.6000	0.7704
A ₃	0.0250	0.3640	0.6525
B ₁	0.0760	1.2010	1.0080
B ₂	0.0500	0.7580	0.8800
B ₃	0.0300	0.4065	0.6950
C ₁	0.0480	0.5760	0.9116
C ₂	0.0300	0.4300	0.7530
C ₃	0.0160	0.2560	0.5561

TABLE 3
Negative Sols

Sol sample	Precipitation values for cations :—		
	Potassium	Barium $\times 10^3$	Aluminum $\times 10^5$
X ₁	0.0060	0.3510	0.5805
X ₂	0.0400	0.5400	0.7620
X ₃	0.0650	0.9125	0.9842
Y ₁	0.0150	0.4025	0.6548
Y ₂	0.0520	0.6050	0.9010
Y ₃	0.0720	0.9580	1.1060
Z ₁	0.0035	0.2000	0.5364
Z ₂	0.0260	0.4700	0.7680
Z ₃	0.5060	0.6050	0.9315

SUMMARY OF THE RESULTS

A perusal of the table 2 & 3, where the positively charged hydrous ferric oxide sols are obtained by different methods, but are at the same pH, the coagulating values of the different electrolytes for the infinite time of observation, will show that the stability of these sols is in the order sol B > sol A > sol C. It is, therefore, clear that the nature and the behaviour of the various sols prepared by different methods differ remarkably including its stability towards electrolytes. It is evident that the sols prepared by peptising the hydrous oxide by an acid is more stable. The surface forces operating in aggregation process is also of importance in defining the stability of a sol, which is obviously different for the sol particles obtained by different methods. Indeed, the coagula of hydrous ferric oxide sols from Krecke's sol is more compact than that obtained from other sols samples, where the coagula are highly flocky and have a tendency to yield a gel like structure.⁰

In the case of negatively charged sols, the stability is in the order Y > X > Z. Here, it is of interest to note that all the sol samples, have a common peptising (OH), though stabilised by arsenious oxide, glucose and glycerol respectively. The sol which is stabilised by glucose, is found to be most stable. The stabilising power of glycerol has been found to be poor as is evident from the fact that the larger amounts of it are needed to obtain a sol of measurable stability.

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REFERENCES

1. Cf. Chatterjee and Dhar, N. R., *Chem. News.*, 121, 253 (1920).
2. Dumanskiiond Shershrev, *J. Russ. Phys. Chem. Soc.* 62, 187 (1930).
3. Graham, *J. Chem. Soc.*, 51, 249, (1862); *Phil. Trans.*, 151, 208 (1961).
4. Grimaux, *Compt. Rend.* 98, 1485 (1884).
5. Jirgensons, *Kolloid-Z.*, 44, 203 (1928); Bautaric; *Bull. Sci. Acad. roy. Belg.* (5), 10, 560 (1924); Hilderbrand and Sorum., *J. Phys. Chem.*, 38, 809 (1934).
6. Krecke, *J. prakt. Chem.*, (2), 3, 286, 295 (1871).
7. Kruyt, H. R. and Van Arkel., M., *Rev. Trav. Chim.*, 39, 656 (1920); *Kolloid-Z.*, 32, 29 (1923).
8. Mukerjee, J. N., and coworkers., *J. Chem. Soc.*, 115, 461 (1919).
9. Nand K. C., Prasad G. and Ghosh. S., *Proc. Natl. Acad. Sci. India*, 33, 9 (1963).
10. Ottewill, R. H., and Watanabe., A., *Kolloid-Z.*, 170, 38 (1960).
11. Pean De. st. Gilles., *Compt. rend.*, 40, 568, 1243 (1855).
12. Rose, *Ann. Chim. Phys.*, 24, 27 (1823).
13. Vogel, I. A., A text book of Quantitative Inorganic analysis, IInd Edn., Longmans, page 296.
14. Vogel, I. A., A textbook of Quantitative Inorganic analysis, IInd Edn., Longmans, page 258.
15. Weiser, H. B., Inorganic Colloid. Chem., Vol. II., John Wiley and Sons, London, (1935) page 65.
16. Westgren, A. and Reitstotter, J., *J. Phys. Chem.*, 26, 537 (1922).

STABILITY OF LYOPHOBIC COLLOIDS—PART V THE DIELECTRICAL PROPERTIES OF THE NON-ELECTROLYTES AND WATER MIXTURES

By

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ABSTRACT

The dielectric constant of the dispersing medium has a great bearing on the stability of the lyophobic sols. The value of the mixtures of colloidal solution with the electrolyte and non-electrolyte is not easily determinable as it is a function of number of variables, therefore, such values become hardly dependable. However, it has been possible to find these values for the mixtures of non-electrolyte and water within the estimated accuracy. In the coagulation studies at varying dielectric constants of the dispersing medium, it has become necessary to employ activity instead of the precipitating concentrations. Theoretically it has been possible to assess the active masses of the precipitating ions, within the approximations of the validity of the modified Debye-Huckel theory for electrolytic solution. This paper deals with the determination of the dielectric constant of the mixtures of the dioxane or formamide with water at different temperatures and the calculation of the active masses of some electrolytes in the solvents of the different dielectric constants for evaluating the true precipitation values for electrolytes in the coagulation studies reported in the subsequent papers.

Variation of the dielectric constant by the addition of a non-electrolyte has been emphasised to control the stability of lyophobic sol.^{8,19} We have already reported¹⁶ that the stability of the hydrous ferric oxide sols is found to show a considerable variation with an alteration in the values of dielectric constant of the dispersing medium, as affected by either dioxane or formamide. However, it is desirable to consider the net change in the property for the mixtures of the non-electrolyte, electrolyte and the colloidal solution, but the experimental procedure unfortunately did not permit this evaluation. The determination of the dielectric constant for a colloidal solution alone involves the consideration of several factors. If there is a considerable difference in the dielectric constant or conductivity between the dispersoid and the dispersing medium, interfacial polarization causes dielectric loss and frequency dependence of the dielectric constant in the low frequency region. In aqueous colloidal solutions, the presence of electrolyte essential for peptization, causes sufficient conductivity difference giving rise to interfacial polarization. The electric double layer at the particle surface and its possible distortion by an electrical field is an additional complication. Thus, the dispersoid may acquire a dipole moment causing a variation in the dielectric constant. Further, hydration or solvation may have influence on the dielectric constant because hydration is under the influence of strong adsorption forces leading to a decrease of the dielectric

constant, owing to the fixation of the molecules. Thus, the influence of several factors need to be taken into consideration, in the interpretation of the dielectric constant measurements of the colloidal systems, as has been pointed out by Kruyt and Overbeek¹², Winener²⁰, and others^{3,7}.

It has been shown that the dielectric constant of aqueous solution of electrolytes are little different from those of pure water^{6,19}. Accurate measurements on N/270 and N/70 solutions of potassium chloride by Drake, Piece and Dew⁴, and Wymann²¹ have shown that the values differed from that of distilled water by less than 1%. Hasted, Ristson and Collie¹⁰ have drawn attention to the role of the hydration of the ions such that for higher ionic concentration, where the values of the dielectric constant may be lowered than in the case of dilute solution.

In view of what has been said, the role of the non-electrolyte affecting the dielectric constant has only been taken into consideration here as the effect of the electrolytes added to the sol is rather small. Investigation described here, deals with sols obtained by different methods, hence, no attempt has been made for determining this value for the various sols and electrolyte mixtures and only the measurements of the dielectric constant of the aqueous solution of non-electrolyte have been made or calculated as these values are based on dependable methods, and these we shall now record below.

(i) *Dielectric constant of dioxane water mixtures.* The values of the dielectric constant of dioxane water mixtures were experimentally determined with the help of Dilekometer at $(25 \pm 0.01)^\circ\text{C}$. These values obtained by us agreed well with those of Akerlof and Short² measured by a resonance method at a wavelength of 150 m for the large range of temperature, for a series of dioxane-water mixtures. Akerlof¹ suggested the equation (1) to express his data for a mixture at different temperature within the estimated accuracy.

$$\log \epsilon = \log a - b \cdot t \quad (1)$$

where ' ϵ ' is the dielectric constant of the dioxane-water mixtures, a and b are the empirical constants differing for different mixtures at various temperatures t and from the values of a and b given by Akerlof and Short (*loc. cit.*), the values of ϵ for dioxane-water mixtures have been calculated for different temperatures. The values of these constant for 5% dioxane in water are not available from the data of Akerlof but it is seen from his data that the value of the constant b approaches the value of 0.002, for pure water, which is the temperature coefficient α for the dielectric constant changes with temperature for pure water, as given by the relation,¹⁵

$$\log \epsilon_{t'} = \log \epsilon_t - \alpha (t' - t) \quad (2)$$

where $\epsilon_{t'}$ and ϵ_t are the dielectric constant of dioxane-water mixture at temperatures t' and t respectively. Hence, the above relation have been used for 5% of

dioxane-water mixture without introducing any appreciable error. The data obtained by Akerlof (*loc. cit.*) show that the dielectric constant of dioxane-water mixtures decrease almost linearly with the increasing percentage of dioxane upto 50% by weight but beyond this, the decrease becomes less than linear relationship. In the present study only 40% of dioxane was employed. The values of 'c' for dioxane water mixtures, employed in my experiments (obtained as described earlier) are tabulated below:—

TABLE I
Values of Dielectric Constant of Dioxane Water Mixtures

Dioxane wt. %	TEMPERATURE							
		25°C		30°C		35°C		40°C
	(**)							
5	72.85	-		71.19		69.56		67.98
10	69.72	69.69		67.98		66.33		64.71
20	61.14	60.79		59.24		57.73		56.24
30	51.48	57.90		50.52		49.90		47.88
40	43.32	42.98		41.71		40.66		39.55

In the above table, column second (**) gives the values as determined by us, which agrees well with the calculated values within reasonable limits.

(ii) *Dielectric constant of formamide-water mixtures.* The dielectric constant of formamide water mixtures could not be measured, due to the limitations of the availability of apparatus, specially because solution showed some conductance. Hence, these values were calculated by equation (5) Lichtenecker¹³ and Lowry¹⁴ represented the dielectric constant of the mixtures as a function of the dielectric constant and concentrations of the individual nonpolar components of the mixtures and this is calculable from its density and polarization by the expression :—

$$P_{1,2} = C_1 P_1 + C_2 P_2 \quad (3)$$

where C_1, C_2 are the concentrations and P_1, P_2 are the polarisation of the components. Further Onsager¹⁵ has shown that for the dilute solutions the dielectric constant is a linear function of the number of polar molecules per ml., of the solution Kirwood¹¹, has shown that for the dilute aqueous solutions of proteins and amino acids the dielectric constant may be given as—

$$\epsilon = \epsilon_1 + k \cdot C \quad (4)$$

where ϵ_1 is the dielectric constant of the pure solvent, C refers to the concentration of the solute expressed in moles per litre and k is a constant.

We have, here calculated, the dielectric constant of formamide and water mixtures, assuming that there is no interaction of formamide with water and that the total dielectric constant of the mixture is equal to the sum of the contributions made by each components. Thus, ϵ of the aqueous solutions of formamide, becomes,

$$\epsilon = \epsilon_1 f_1 + \epsilon_2 f_2 \quad (5)$$

where ϵ_1 is the dielectric constant of water and f_1 its mole fraction, and ϵ_2, f_2 refer to those for formamide. Formamide, water mixtures were prepared by mixing

appropriate volumes of formamide and water. Their mole fractions were calculated, from their standard values of the densities at different temperatures. In the table (2) are given the calculated values of the mole fractions of formamide and water.

TABLE 2

Formamide wt. %	WATER (f_1)				FORMAMIDE (f_2)			
	TEMPERATURE							
	25°C	30°C	35°C	40°C	25°C	30°C	35°C	40°C
5	0.9769	0.9763	0.9765	0.9769	0.0232	0.0230	0.0235	0.0231
10	0.9521	0.9523	0.9524	0.9525	0.0278	0.0476	0.0476	0.0476
20	0.8983	0.8985	0.8987	0.8988	0.1017	0.1015	0.1013	0.1012
30	0.8372	0.8378	0.8383	0.8386	0.1628	0.1622	0.1617	0.1614
40	0.7680	0.7685	0.7689	0.7693	0.2320	0.2315	0.2311	0.2307

Variation of dielectric Constant with Temperature. The values of the dielectric constant of pure formamide and pure water have been evolved at higher temperatures with the help of following equations (6) & (7)

$$\epsilon_t' = \epsilon_t - 0.72 (t' - t) \quad (6)$$

$$\log_{10} \epsilon_t' = \log_{10} \epsilon_t - 0.002 (t' - t) \quad (7)$$

(where, ϵ_t' and ϵ_t refer to the dielectric constant at t' and t °C respectively).

respectively (ϵ^{15}) and these values are reproduced in the table (3).

TABLE 3

The Values of Dielectric Constant of Formamide and Water at Different Temperatures

Liquid	Values of dielectric constant at :—				
	20°C	25°C	30°C	35°C	40°C
Water					
(ϵ_1)	80.36	78.54	76.76	75.01	73.30
Formamide					
(ϵ_2)	109.00	105.40	101.80	98.20	94.60

The dielectric constant of the mixtures of formamide and water have been calculated by the equation (5) cited earlier and these values are summed up in the table below :

TABLE 4
Dielectric Constant of Formamide-water Mixtures at Different Temperature

Formamide wt. %	Values of the dielectric constant at :			
	25°C	30°C	35°C	40°C
0	78.54	76.76	75.01	73.30
5	79.16	77.32	75.56	73.79
10	80.81	77.92	76.13	74.31
20	81.27	79.29	77.30	75.46
30	82.91	80.88	78.05	76.75
40	84.77	82.54	80.39	78.52

In our coagulations studies (*vide*¹⁰, it was considered necessary to employ the actual active mass of the precipitating ions, instead of their concentration needed for coagulation as the dielectric constant has been widely varied. The active masses of an electrolyte at any concentration have been calculated from the activity coefficient⁹ given by the relation :

$$-\log f_{\pm} = A \cdot Z + Z - \sqrt{\mu} - C' \mu \quad (8)$$

The value of A for the medium of the dielectric constant ϵ_1 at the absolute temperature T_1 have been calculated from the relation

$$A = \left(\frac{0.509 (78.54 \times 298)^{3/2}}{(\epsilon_1 T_1)^{3/2}} \right) \quad (9)$$

These calculated values of A for different ϵ and temperature are given in the table (5).

TABLE 5
Values of 'A' for Different Dielectric Constant at Different Temperature

FORMAMIDE									DIOXANE			
(*) (*)									(*) (*)			
% of (*) (*)	(TEMPERATURE)°C											
	25	30	35	40	25	30	35	40				
0	0.5090	0.5140	0.5189	0.5242	—	—	—	—				
5	.5032	.5083	.5135	.5193	0.5699	0.5754	0.5811	0.5872				
10	.4873	.5025	.5075	.5137	.6089	.6166	.6240	.6323				
20	.4835	.4896	.4952	.5021	.7476	.7480	.7686	.7805				
30	.4691	.4752	.4889	.4895	.9475	.9623	.9770	.9936				
40	.4538	.4608	.4677	.4731	1.1257	1.1283	1.1300	1.1323				

These values were employed for the calculation of the activity coefficient, hence, the active mass of the various precipitating ions. In equation (8) C is a constant approximately equal to $(Z_+ \cdot Z_- \cdot a \cdot A \cdot B + C)$, here ' a ' is the particle radius, C is a constant to be derived empirically and B is made up of universal constant, the dielectric constant and the temperature, for water at 25°C its value comes to 3.29×10^7 . Theoretical interpretation of a and C at such high concentrations ($\mu > 10^{-1}$) are difficult to make, because of several effects, which superimpose on each other, at such concentrations.⁹ However, the relation (8) gives the activity coefficient for concentrated solution ($\mu > 10^{-2}$) but the calculated values become less exact because of the failure of the applicability of this relation as well, because, when the dielectric constant is sufficiently lowered, the interionic attraction energy increases as inverse function of $\epsilon^{3/2}$ and increasing tendency of the formation of ions pairs. It should, however, be mentioned here that the values of activity are at least correct within these approximations, and that such values have been utilised for a comparative study only.

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REFERENCES

1. Akerlof, *J. Am. Chem. Soc.*, 54, 4125 (1932).
2. Akerlof, and Short, *Ibid.*, 58, 1241 (1936).
3. Clark, C. H. D., *The fine structure of matter*, Wiley, New York. 1938, Vol. II. Part II, page 240.
4. Cf. Darke, Piece, and Dew., *Phys. Rev.*, 35, 613 (1930).
5. Debye, P., and Huckel, E., *Physik. Z.*, 24, 185 (1923); 25, 97 (1924).
6. Falkenhagen, H., *Electrolytes*, Oxford; London, Chap. IX (1934).
7. Freundlich, H., *Kopillarchemie*. Akademische—Verlagsgesellschaft. m.b.h. Leipzig, (1932), Vol. II, page 62 and 333.
8. Freundlich, H., *Colloid and Capillary, Chem.* (Mathuen, London), 463, 420 (1926); *Z. Physik. Chem.* 44, 135 (1903).
9. Granwall, T. H., LaMer, V. K., *et al.* *Phys. Z.* 29, 358 (1928); *J. Phys. Chem.* 35, 2345 (1931).
10. Hasted, J. B., Ritson, D. M. and Colloc. C. H., : *J. Chem. Phys.*, 16, 1 (1948).
11. Kirkwood, *Vide*: Symth : *Dielectric behaviour and structure*. Mc. Gray. Hill, Book Company. Edn. (1955), page 392, Eq. (2.1.).
12. Kruyt, H. R. and Overbeck, J. Th. G., *Kolloid-Z.*, 81, 257 (1937).
13. Lichtenacker, H., *Physik.*, 27, 115 (1926).
14. Lowary, H. H., *J. Franklin. Inst.*, 203, 413 (1927).
15. Maryott, A. A. and Smith, E. R. : *vide* : Table of dielectric constant of pure, liquids, National Bureau of Standards, Circular 514, issued, August, 10 (1951).
16. Nand K. C. and Ghosh S. : *Proc., Natl. acad. Sci., India*, 34-A, 78 (1964).
17. Onsager, L., *J. Am. Chem. Soc.*, 58, 1486 (1936).
18. Ostwald, Wo ; *Grandrissder Kolloid Chemie.*, 441 (1909) and subsequent publications.
19. Wein, M., *Ann. Physik.*, 22, 98 (1924) : *Ibid.*, 44, 256 (1927).
20. Wiener, O. *Abhandl. Math. Phys. Klasse. Sach. Akad. Wiss. Leipzig*. 32, 507, (1912); cf Brug-gemen, *Ann. Physik*, (5) 24, 636 (1935).
21. Wymann, J., *Phys. Rev.*, 35, 623 (1930).

ON SOME ARITHMETICAL PROPERTIES OF BERNOULLI'S AND EULER'S GENERALISED POLYNOMIALS

By

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ABSTRACT

Carlitz (1) has considered the properties of the product of the Bernoulli's and Euler's generalised polynomials. Here new arithmetical properties of Bernoulli's and Euler's generalised polynomials will be found.

The generating functions of Bernoulli's and Euler's generalised polynomials are given as follows :—

$$\left(\frac{t}{e^t - 1} \right)^p e^{xt} = \sum_{m=0}^{\infty} B_m^p(x) \frac{t^m}{m!} \quad \dots \quad (A)$$

$$\text{and } \left(\frac{2}{e^t + 1} \right)^p e^{xt} = \sum_{m=0}^{\infty} E_m^p(x) \frac{t^m}{m!} \quad \dots \quad (B)$$

Differentiating (A) with respect to x and equating the coefficients of t^m from both sides we have

$$D. B_m^p(x) = m B_{m-1}^p(x) \quad \dots \quad (1)$$

similarly $D. E_m^p(x) = m E_{m-1}^p(x)$ where $D = \frac{d}{dx}$

Differentiating both sides of (A) with respect to t and applying (1) we have

$$\begin{aligned} B_{m+1}^p(x+1) &= \frac{1}{[p]} [p-m+x] D [p-1-m+(x-1)D] \dots \\ &\dots [1-m+(x-p+1)D] B_m(x-p+1) \quad \dots \quad (2) \end{aligned}$$

$$\begin{aligned} \text{similarly } E_{m+1}^p(x+1) &= \frac{2^p}{[p]} \left[\frac{x}{m+1} D - 1 \right] \left[\frac{x}{m+2} D - 1 \right] \dots \\ &\dots \left[\frac{x}{m+p+1} D - 1 \right] E_{m+p-1}^p(x) \quad \dots \quad (3) \end{aligned}$$

$$\text{Again } \left(\frac{t}{e^t - 1} \right)^p \cdot e^{xt} \left[1 - e^{r/2k} e^{2t/2k} - \dots + (-1)^{2k-1} e^{\frac{2k-1}{2k} t} \right]$$

$$= \sum_{m=0}^{\infty} \frac{t^m}{m!} \left[\sum_{r=0}^{2k-1} (-1)^r B_m^{(p)} \left(x + \frac{r}{k} \right) \right]$$

$$\text{Hence } \sum_{m=0}^{\infty} \frac{t^m}{m!} \left[\sum_{r=0}^{2k-1} (-1)^r B_m^{(p)} \left(x + \frac{r}{2k} \right) \right]$$

$$= \frac{-t e^t}{e^{2k+1} - 1} \left(\frac{t}{e^t - 1} \right)^{p-1}$$

$$= -\frac{1}{2} \sum_{m=0}^{\infty} E_m(2kx) \left(\frac{t}{2k} \right)^m \frac{1}{m!}$$

$$\times \sum_{n=0}^{\infty} B_n^{(p-1)}(0) \frac{t^{n+1}}{(n+1)!}$$

$$\text{Hence } 2 \sum_{r=0}^{2k-1} (-1)^r B_m^{(p)} \left(x + \frac{r}{k} \right) + m \frac{E_{m-1}(2kx)}{(2k)^{m-1}} B_0^{(p-1)}(0)$$

$$+ \frac{m(m-1)}{1!} \cdot \frac{E_{m-2}(2kx)}{(2k)^{m-2}} B_1^{(p-1)}(0) + \dots + E_0(2kx) B_{m-1}^{(p-1)}(0) = 0$$

$$\text{or } 2 \sum_{r=0}^{2k-1} (-1)^r B_m^{(p)} \left(x + \frac{r}{k} \right) + m \sum_{r=0}^{m-1} \frac{E_{m-1-r}(2kx)}{(2k)^{m-1-r}} B_r^{(p-1)}(0) = 0 \quad \dots (4)$$

$$\text{Now } \left(\frac{2}{e^t + 1} \right)^p \sum_{r=0}^{2k-1} e^{t(x+r/2k)} = \sum_{m=0}^{\infty} \frac{t^m}{m!} \left\{ \sum_{r=0}^{2k-1} E_m^{(p)} \left(x + \frac{r}{2k} \right) \right\}$$

$$\sum_{m=0}^{\infty} \frac{t^m}{m!} \left\{ \sum_{r=0}^{2k-1} E_m^{(p)} \left(x + \frac{r}{2k} \right) \right\}$$

$$= \left(\frac{2}{e^t + 1} \right)^p \cdot e^{tx} \left[1 + e^{\frac{t}{2k}} + e^{\frac{2t}{2k}} + e^{\frac{2k-1}{2k} t} + \dots \right]$$

$$\begin{aligned}
&= \left(\frac{2}{e^t + 1} \right)^p \cdot e^{tx} \frac{e^t - 1}{e^{t/2k} - 1} \\
&= \left(\frac{2}{e^t + 1} \right)^p \left[\frac{e^{t(x+1)}}{e^{t/2k} - 1} - \frac{e^{tx}}{e^{t/2k} - 1} \right] \\
&= \sum_{m=0}^{\infty} \frac{t^m}{m!} E_m^p(0) \left[\sum_{n=0}^{\infty} B_n\{2k(x+1)\} \left(-\frac{t}{2k} \right)^{n-1} \frac{1}{n!} - \right. \\
&\quad \left. \sum_{n=0}^{\infty} B_n(2kx) \left(-\frac{t}{2k} \right)^n \right]
\end{aligned}$$

Therefore

$$\begin{aligned}
&\frac{\sum_{r=0}^{2k-1} E_m^p \left(x + \frac{r}{2k} \right)}{m!} = \frac{E_{m+1}^p(0)}{(m+1)!} B_0\{2k(x+1)\} \\
&+ \frac{F_m^p(0)}{m!} \cdot \frac{B_1\{2k(x+1)\}}{(2k) \cdot 1!} + \frac{E_{m-1}^p(0) \cdot B_2\{2k(x+1)\}}{(m-1)! (2k)^2 \cdot 2!} \times \\
&- \frac{1}{m!} E_m^p(0) B_0(2kx) - \frac{1}{(m-1)!} E_{m-1}^p(0) \cdot \frac{B_1(2kx)}{(2k)} \\
&- \frac{1}{(m-2)!} E_{m-2}^p(0) \cdot \frac{B_2(2kx)}{2! (2k)^2} - \dots \\
&= \frac{1}{m+1} \sum_{r=0}^{m+1} E_{m+1-r}^p(0) {}^{m+1}C_r \frac{B_r\{2k(x+1)\}}{(2k)^r} \\
&- \sum_{r=0}^m E_{m-r}^p(0) {}^mC_r \frac{B_r(2kx)}{(2k)^r} \dots (5)
\end{aligned}$$

The following results are evident

... (5)

$$B_m^{2p}(x+y) = \sum_{r=0}^m {}^mC_r B_{m-r}^p(x) B_r^p(y)$$

... (6)

$$E_m^{2p}(x+y) = \sum_{r=0}^m {}^m C_r E_{m-r}^p(x) E_r^p(y)$$

$$B_m^p(x) = \frac{1}{2^m} \sum_{r=0}^m {}^m C_r B_{m-r}^p(x) \cdot E_r^p(x) \quad \dots (7)$$

$$B_m^p(x) = \sum_{r=0}^m {}^m C_r B_r^p(0) x^{m-r} \quad \dots (8)$$

$$E_m^p(x) = \sum_{r=0}^m {}^m C_r E_r^p(0) x^{m-r} \quad \dots (9)$$

$$B_m^{p+q}(2x) = \sum_{r=0}^m {}^m C_r B_{m-r}^p(x) \cdot B_r^q(x) \quad \dots (10)$$

If $m \geq 0$, utilising (1) we have

$$\int_0^1 x^n B_m^p(x) dx = \frac{B_{m+1}^p(1)}{(m+1)} - \frac{n \cdot B_{m+2}^p(1)}{(m+1)(m+2)} + \dots$$

$$+ \frac{(-1)^n \frac{n}{n!}}{(m+1)(m+2) \dots (m+n+1)} \left\{ B_{n+m+1}^{p(1)} - B_{n+m+1}^{p(0)} \right\} \dots (11)$$

$$\int_0^1 x^n E_m^p(x) dx = \frac{E_{m+1}^p(1)}{(m+1)} - \frac{n \cdot E_{m+2}^p(1)}{(m+1)(m+2)} + \dots$$

$$+ \frac{(-1)^n \frac{n}{n!}}{(m+1)(m+2) \dots (m+n+1)} \cdot \left\{ E_{n+m+1}^{p(1)} - E_{n+m+1}^{p(0)} \right\} \quad (12)$$

$$\int_0^1 B_n^p(x) \cdot B_m^p(x) dx = \frac{1}{(m+1)} C_{m+1,n} - \frac{n}{(m+1)(m+2)} C_{m+2,n-1}$$

$$+ \frac{(-1)^n \frac{n}{n!}}{(m+1)(m+2) \dots (m+n)} C_{m+n+1,n}^{(0)}$$

where $C_{m+1, n} = B_{m+1}^{(p)}(1) \cdot B_n^{(p)}(1) - B_{m+1}^{(p)}(0) \cdot B_n^{(p)}(0)$... (13)

$$\begin{aligned} & \int_0^1 E_m^{(p)}(x) \cdot E_n^{(p)}(x) dx \\ &= \frac{1}{m+1} C_{m+1, n}^1 - \frac{n}{(m+2)(m+1)} C_{m+2, n-1}^1 + \dots \\ &+ \frac{(-1)^n \frac{1}{m}}{(m+1)(m+2) \dots (m+n)} \cdot C_{m+n+1, 0}^1 \end{aligned}$$

where $C_{m+1, n}^1 = E_{m+1}^{(p)}(1) E_n^{(p)}(1) - E_{m+1}^{(p)}(0) E_n^{(p)}(0)$.

REFERENCE

1. Carlitz, L., Multiplication formulas for generalised Bernoulli's and Euler's Polynomials, *Duke. Math. Jour.*, 27, 537 (1960).

SOME INTEGRALS INVOLVING E-FUNCTION OF MACROBERT AND G-FUNCTION OF MEIJER

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ABSTRACT

In this work some integrals involving the product of E. function of MacRobert and G function of Meijer have been evaluated. The technique adopted is based on the use of operational calculus. The results obtained are important as they involve the well known functions, and the method employed illustrates the use of operational calculus in evaluating integrals which are otherwise difficult to evaluate. A result of Varma is also generalised. The following results have been obtained in this paper

$$\begin{aligned}
 1. \int_0^{\infty} x^{-\nu-1} E(\rho; \alpha_r; q; \rho_s; x^m) E(\mu, \delta :: xy) dx \\
 = \frac{1}{2^{3/2(m-1)}} \frac{1}{\{\Gamma(\frac{1}{2})\}^{3m-3}} \frac{\mu + \delta - \nu - 3/2}{y^{\nu}} \times \\
 \sum_{r=1}^{p+m} \frac{\pi}{q} \frac{\Gamma(\alpha_s - \alpha_r) \Gamma(\alpha_r)}{\Gamma(\rho_s - \alpha_r)} \cdot \frac{\pi}{R=0} \Gamma\left(\alpha_r + \frac{\delta - \nu + R}{m}\right) \Gamma\left(\alpha_r + \frac{\mu - \nu + R}{m}\right) \times \\
 \left(\frac{m}{y}\right)^{m\alpha_r} \frac{q+1+2m}{p+m-1} \left[\begin{matrix} \alpha_r, \alpha_r - \rho_1 + 1, \dots, \alpha_r - \rho_q + 1, \beta_0 \dots \beta_{m-1}, \theta_0 \dots \theta_{m-1}; \\ \alpha_r - \alpha_1 + 1, \dots, \alpha_r - \alpha_{p+m} + 1 \end{matrix} \right] \\
 (-1)^{p+m-q} \left(\frac{m}{y}\right)^m \Big]
 \end{aligned}$$

where $\beta_R = \left(\alpha_r + \frac{\delta - \nu + R}{m} \right)$

$\theta_R = \left(\alpha_r + \frac{\mu - \nu + R}{m} \right) \quad R=0, \dots, m-1.$

$$\begin{aligned}
2. \quad & \int_0^{\infty} t^{-\alpha} E\left(\mu, \delta; -\frac{1}{t+a}\right) G_{pq}^{mn}\left(zt \left| \begin{matrix} a_1 \dots a_p \\ b_1 \dots b_q \end{matrix} \right. \right) dt \\
& = \sum_{r=0}^{\infty} \frac{(-1)^r a^r}{r!} G_{p+1, q+2}^{m+2, n+1}\left(z \left| \begin{matrix} \alpha, a_1 \dots a_p \\ \alpha+\mu+r-1, \alpha+\delta+r-1, b_1 \dots b_q \end{matrix} \right. \right) \\
3. \quad & \int_0^{\infty} t^{-(\alpha+3/2)} e^{-\frac{1}{2t}} G_{pq}^{mn}\left(\frac{t}{z} \left| \begin{matrix} a_1 \dots a_p \\ b_1 \dots b_q \end{matrix} \right. \right) \left[I_{\nu/2-\frac{1}{2}}\left(\frac{1}{2t}\right) - \right. \\
& \quad \left. \times I_{\nu/2+\frac{1}{2}}\left(\frac{1}{2t}\right) \right] dt \\
& = \frac{2}{\sqrt{\pi}} G_{p+1, q+2}^{m+1, n+1}\left(z \left| \begin{matrix} \alpha, a_1 \dots a_p \\ \alpha+\frac{\nu}{2}, b_1 \dots b_q, \alpha-\nu/2 \end{matrix} \right. \right)
\end{aligned}$$

1. *Introduction.*—The object of this paper is to evaluate some integrals involving the E-function and the G-function. The technique employed is based on the use of operational calculus. In section 2 an integral involving product of E-functions has been evaluated. In section 3 integrals involving G-function have been evaluated.

$f(x) \supset \phi(p)$ means that $\phi(p)$ is the Laplace transform of $f(x)$ i.e. they are connected by the integral equation

$$\phi(p) = p \int_0^{\infty} e^{-px} f(x) dx, \quad \text{Re}(p) > 0.$$

We shall be using the results given underneath.

If $f(x) \supset \phi(p)$ then

$$e^{-ax} f(x) \supset \frac{p}{p+a} \phi(p+a) \quad (1.1)$$

If $f(x) \supset \phi(p)$ and

$\Psi(x) \supset F(p)$ then

$$\int_0^{\infty} f(x) F(x) \frac{dx}{x} = \int_0^{\infty} \phi(p) \Psi(p) \frac{dp}{p} \quad (1.2)$$

provided the integrals converge. In future this result will be called "Goldstien's theorem."

2. We have from Ragab [2] the operational relation

$$x^{v-1} E(p; \alpha_r; q; f_s; x^{-m}) \supset (2\pi)^{\frac{1-m}{2}} m^{v-\frac{1}{2}} P^{1-v} E(p+m; \alpha_r; q; p_s; m^{-m} P^m) \quad (2.1)$$

where $\alpha_{p+k} = \frac{v+k-1}{m}$, $(k = 1, 2, \dots, m)$

$R(v) > 0$ and $p > q + 1$

From [4] we have

$$2(yx)^{\frac{\mu+\delta}{2}-1} K_{\delta-\mu}(2\sqrt{yx}) \supset \frac{p}{y} E\left(\mu, \delta; \frac{y}{p}\right) \quad (2.2)$$

$R(p) > 0$ $R(\mu) > 0$ $R(\delta) > 0$

Applying Goldsteid's theorem to (2.1) and (2.2) we get

$$\int_0^\infty x^{-v-1} E(p; \alpha_r; q; p_s; x^m) E(\mu, \delta; yx) dx \\ 2m^{v-\frac{1}{2}} (2\pi)^{\frac{1-m}{2}} y^{\frac{\mu+\delta}{2}} \int_0^\infty t^{\frac{1}{2}(\mu+\delta)-v-1} K_{\delta-\mu}(2\sqrt{yt}) E(p+m; \alpha_r; q; p_s; \\ m^{-m} t^m) dt \quad (2.3)$$

where $R(m\alpha_r - v + \delta) > 0$, $R(m\alpha_r - v + \mu) > 0$, $r = 1, \dots, p$; $R(\mu) > 0$, $R(\delta) > 0$, $R(v) > 0$

Substituting the expansion of E-function in the t -integral and inverting the order of integration and summation which is justifiable, the r. h. s. of (2.3) becomes

$$2m^{v-\frac{1}{2}} (2\pi)^{\frac{1-m}{2}} y^{\frac{\mu+\delta}{2}} \sum_{r=1}^{p+m} \frac{\frac{p+m}{\pi} \Gamma(\alpha_s - \alpha_r) \cdot \Gamma(\alpha_r)}{\frac{q}{\pi} \Gamma(\rho_t - \alpha_r)} \frac{1}{m^{\alpha_r}} \times \\ \int_0^\infty t^{\frac{1}{2}(\mu+\delta)-v+m\alpha_r-1} K_{\delta-\mu}(2\sqrt{yt}) {}_qF_{p+m-1} \\ \left[\begin{matrix} \alpha_r, \alpha_r - \rho_1 + 1, \dots, \alpha_r - \rho_q + 1 \\ \alpha_r - \alpha_1 + 1, \dots, \alpha_r - \alpha_{p+m} + 1 \end{matrix} ; (-1)^{p+m-q} \left(\frac{t}{m}\right)^m \right] dt \quad (2.4)$$

Now expanding the hypergeometric series in (2.4) and integrating term by term with the help of the known result [1p331] viz :—

$$\int_0^{\infty} \frac{x^{s-1}}{x} K_{\nu}(ax) dx = a^{-s} 2^{s-2} \Gamma\left(\frac{s+\nu}{2}\right) \Gamma\left(\frac{s-\nu}{2}\right) \quad (2.5)$$

we get on little simplification

$$= \frac{1}{2^{\frac{m-1}{2}}} \left\{ \Gamma\left(\frac{1}{2}\right) \right\}^{m-1} m^{\nu-\frac{1}{2}} y^{\nu} \sum_{r=1}^{p+m} \frac{\pi}{q} \frac{\Gamma(\alpha_s - \alpha_r) \Gamma(\alpha_r)}{\Gamma(\rho_t - \alpha_r)} \cdot \frac{1}{(my)^{m\alpha_r}} \times$$

$$\sum_{n=0}^{\infty} \frac{(\alpha_r)_n (\alpha_r - \rho_1 + 1)_n \dots (\alpha_r - \rho_q + 1)_n}{(\alpha_r - \alpha_1 + 1)_n \dots (\alpha_r - \alpha_{p+m} + 1)_n} \Gamma(\delta - \nu + m\alpha_r + mn)$$

$$\frac{\Gamma(\mu - \nu + m\alpha_r + mn)}{(-1)^{\frac{p+m-q}{n}} \left\{ \frac{1}{(my)^m} \right\}^n} \quad (2.7)$$

where $(\alpha)_n = \alpha \cdot (\alpha+1) \dots (\alpha+n-1)$

using the result [3 p. 4] viz :

$$\frac{\pi^{m-1}}{R=0} \Gamma\left(z + \frac{R}{m}\right) = (2\pi)^{\frac{1}{2}(m-1)} m^{\frac{1}{2} - m\epsilon} \Gamma(m\epsilon) \quad (2.8)$$

we get

$$\int_0^{\infty} x^{-\nu-1} E(p; \alpha_r; q; \rho_s; x^m) E(\mu, \delta; xy) dx$$

$$= \frac{1}{2^{3/2(m-1)}} \times \frac{1}{\{\Gamma(\frac{1}{2})\}^{3m-3}} \times m^{\mu+\delta-\nu-3/2} y^{\nu} \times$$

$$\sum_{r=1}^{p+m} \frac{\pi}{q} \frac{\Gamma(\alpha_s - \alpha_r) \Gamma(\alpha_r)}{\Gamma(\rho_t - \alpha_r)} \cdot \frac{\pi^{m-1}}{R=0} \Gamma\left(\alpha_r + \frac{\delta - \nu + R}{m}\right) \Gamma\left(\alpha_r + \frac{\mu - \nu + R}{m}\right)$$

$$\left(\frac{m}{y}\right)^{m\alpha_r} \times$$

$$q+1+2m \text{ F } p+m-1 \left[\begin{array}{c} \alpha_r, \alpha_r - \rho_1 + 1, \dots, \alpha_r - \rho_q + 1, \beta_0, \beta_1, \dots, \beta_{m-1}, \theta_0, \theta_1, \dots, \theta_{m-1} \\ \alpha_r - \alpha_1 + 1, \dots \dots \dots \dots \dots \end{array} \right. \\ \left. \alpha_r - \alpha_{p+m} + 1 ; (-1)^{p+m-q} \left(\frac{m}{y} \right)^m \right] \quad (2.9)$$

where $\beta_R = \left(\alpha_r + \frac{\delta - \nu + R}{m} \right)$

$$\theta_R = \left(\alpha_r + \frac{\mu - \nu + R}{m} \right), (R = 0, 1, \dots, m-1)$$

and $p \geq q+m+1$

when $p = q+m+1$ $|y^m| > 2m^m$

$$R(m\alpha_r - \nu + \delta) > 0, \quad R(m\alpha_r - \nu + \mu) > 0 \quad r = 1, 2, \dots, p$$

$$R(\mu) > 0 \quad R(\delta) > 0 \quad R(\nu) > 0$$

Particular case :—If we take $m = 2$ in (2.9) we fall back on a result of Varma [6].

3. We know from [1. p. 222] that

$$t^{-\alpha} G_{pq}^{mn} \left(zt \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) \supset P^\alpha G_{p+1, q}^{m, n+1} \left(\frac{z}{P} \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) \quad (3.1)$$

$$\text{where } p < q, \quad R(\alpha) < R(b_j) + 1 \quad j = 1, 2, \dots, q$$

$$p + q < 2(m+n) \quad |\arg P| < (m+n - \frac{1}{2}p - \frac{1}{2}q) \pi$$

using the result [3. p. 209] viz :—

$$G_{p, q}^{m, n} \left(x^{-1} \left| \begin{array}{c} a_r \\ b_s \end{array} \right. \right) = G_{q, p}^{n, m} \left(x \left| \begin{array}{c} 1 - b_s \\ 1 - a_r \end{array} \right. \right) \quad (3.2)$$

we can write the above operational relation as

$$t^{-\alpha} G_{p, q}^{m, n} \left(zt \left| \begin{array}{c} a_1, \dots, a_p \\ b_1, \dots, b_q \end{array} \right. \right) \supset P^\alpha G_{q, p+1}^{n+1, m} \left(\frac{p}{z} \left| \begin{array}{c} 1 - b, \dots, 1 - b_q \\ 1 - \alpha, 1 - a_1, \dots, 1 - a_p \end{array} \right. \right) \quad (3.3)$$

From [4] we have the operational relation

$$2 t^{\frac{1}{2}(\mu+\delta)-1} K_{\delta-\mu}(2\sqrt{t}) \supset P E\left(\mu, \delta :: \frac{1}{P}\right) \quad (3.4)$$

$$R(\mu) > 0 \quad R(\delta) > 0$$

Applying the rule (1.1) to the above step we get

$$2 e^{-at} t^{\frac{1}{2}(\mu+\delta)-1} K_{\delta-\mu}(2\sqrt{t}) \supset P E\left(\mu, \delta :: \frac{1}{P+a}\right) \quad (3.5)$$

Applying Goldstien's theorem to (3.3) and (3.5)

$$\int_0^\infty t^{-\alpha} E\left(\mu, \delta :: \frac{1}{t+s}\right) G_{pq}^{mn}\left(z \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) dt$$

$$= 2 \int_0^\infty s^{-\alpha} P^{\frac{1}{2}(\mu+\delta)+\alpha-2} K_{\delta-\mu}(2\sqrt{P})$$

$$G_{q, p+1}^{n+1, m}\left(\frac{P}{z} \left| \begin{matrix} 1-b_1, \dots, 1-b_q \\ 1-\alpha, 1-a_1, \dots, 1-a_p \end{matrix} \right. \right) dP \quad (3.6)$$

where $R(\alpha+\mu-a_h) > 0$ $R(\alpha+\delta-a_h) > 0$, $h = 1, 2, \dots, p$

$p+1 < q$, $R(\mu) > 0$ $R(\delta) > 0$ $R(b_j - \alpha) > -1$ $j = 1, 2, \dots, q$

Expanding in the r, h, s integral e^{-aP} in powers of P and inverting the order of integration and summation, which is justifiable, we get the r, h, s of (3.6) to be

$$= 2 \sum_{r=0}^\infty \frac{(-1)^r a^r}{\Gamma(r)} \int_0^\infty P^{\frac{1}{2}(\mu+\delta)+\alpha+r-2} K_{\delta-\mu}(2\sqrt{P})$$

$$G_{q, p+1}^{n+1, m}\left(\frac{P}{z} \left| \begin{matrix} 1-b_1, \dots, 1-b_q \\ 1-\alpha, 1-a_1, \dots, 1-a_p \end{matrix} \right. \right) dP.$$

Evaluating the above integral with the help of the result [3, p. 215], viz:—

$$\int_0^\infty y^{-\alpha} K_\nu(2\sqrt{y}) G_{pq}^{m, n}\left(xy \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) dy$$

$$= \frac{1}{2} G_{p+2, q}^{m, n+2}\left(x \left| \begin{matrix} \alpha - \frac{1}{2}\nu, \alpha + \frac{1}{2}\nu, a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \quad (3.7)$$

$$R\left(b_h \pm \frac{\nu}{2} - \alpha\right) > -1 \quad h = 1, 2, \dots, m \quad ;$$

we get, on using (3.2)

$$\begin{aligned} & \int_0^\infty t^{-\alpha} E\left(\mu, \delta : \frac{1}{t+a}\right) G_{p,q}^{m,n} \left(zt \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) dt \\ &= \sum_{r=0}^\infty \frac{(-1)^r a^r}{r!} G_{p+1, q+2}^{m+2, n+1} \left(z \left| \begin{matrix} \alpha, a_1, \dots, a_p \\ \alpha+\mu+r-1, \alpha+\delta+r-1, b_1, \dots, b_q \end{matrix} \right. \right) \quad (3.8) \end{aligned}$$

where $p+1 < q$, $p+q < 2(m+n)$, $|\arg z| < (m+n-\frac{1}{2}p-\frac{1}{2}q)\pi$

$$R(\alpha + \mu - a_j) > 0 \quad R(\alpha + \delta - a_j) > 0 \quad j = 1, 2, \dots, p$$

$$R(\mu) > 0 \quad R(\delta) > 0 \quad R(b_j - \alpha) > -1$$

Particular case :—In the above result if we put $a=0$ we get

$$\begin{aligned} & \int_0^\infty t^{-\alpha} E\left(\mu, \delta : \frac{1}{t}\right) G_{p,q}^{m,n} \left(zt \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) dt \\ &= G_{p+1, q+2}^{m+2, n+1} \left(z \left| \begin{matrix} \alpha, a_1, \dots, a_p \\ \alpha+\mu-1, \alpha+\delta-1, b_1, \dots, b_q \end{matrix} \right. \right) \quad (3.9) \end{aligned}$$

We have from [1, p. 185] the operational relation

$$J_\nu (2\sqrt{t}) \supset \frac{\sqrt{\pi}}{2} P^{-\frac{1}{2}} e^{-1/2P} \left[I_{\nu/2-\frac{1}{2}}(1/2P) - I_{\nu/2+\frac{1}{2}}(1/2P) \right] \quad (3.10)$$

$$R(\nu) > -2 \quad R(P) > 0.$$

Applying Goldstien's theorem to (3.3) and (3.10) we get

$$\begin{aligned} & \int_0^\infty t^{-(\alpha+3/2)} e^{-1/2t} G_{p,q}^{m,n} \left(\frac{t}{z} \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \left[I_{\nu/2-\frac{1}{2}}(1/2t) - I_{\nu/2+\frac{1}{2}}(1/2t) \right] dt \\ &= \frac{2}{\sqrt{\pi}} \int_0^\infty y^{-(1-\alpha)} J_\nu (2\sqrt{y}) G_{q, p+1}^{n+1, m} \left(zy \left| \begin{matrix} 1-b_1, \dots, 1-b_q \\ 1-\alpha, 1-a_1, \dots, 1-a_p \end{matrix} \right. \right) dy \quad (3.11) \end{aligned}$$

$$R(b_j - \alpha) > -\frac{1}{2}, j = 1, 2, \dots, q,$$

$$p < q-1, \quad p+q < 2(m+n), \quad |\arg z| < (m+n-\frac{1}{2}p-\frac{1}{2}q)\pi$$

$$R(\alpha + \nu/2 - a_j) > -1, j = 1, 2, \dots, p, \quad R(\nu) > -2.$$

Using the known integral [3. p. 214] viz:—

$$\int_0^\infty x^{-\alpha} J_\nu(2\sqrt{x}) G_{p,q}^{m,n} \left(xy \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) dx$$

$$= G_{p+2,q}^{m,n+1} \left(x \left| \begin{matrix} \alpha - \frac{1}{2}\nu, a_1, \dots, a_p, \alpha + \frac{1}{2}\nu \\ b_1, \dots, b_q \end{matrix} \right. \right)$$

$$\text{where } R(-\alpha + \frac{1}{2}\nu + b_h) > -1 \quad h = 1, 2, \dots, m;$$

$$R(-\alpha + a_j) < \frac{1}{2} \quad j = 1, 2, \dots, n$$

we get from (3.11) on applying (3.2)

$$\begin{aligned} & \int_0^\infty -(\alpha + 3/2) e^{-1/2t} G_{p,q}^{m,n} \left(t/z \left| \begin{matrix} a_1, \dots, a_p \\ b_1, \dots, b_q \end{matrix} \right. \right) \left[I_{\nu/2-\frac{1}{2}}(1/2t) - \right. \\ & \quad \left. I_{\nu/2+\frac{1}{2}}(1/2t) \right] dt \\ & = \frac{2}{\sqrt{\pi}} G_{p+1,q+2}^{m+1,n+1} \left(z \left| \begin{matrix} \alpha, a_1, \dots, a_p \\ \alpha + \nu/2, b_1, \dots, b_q, \alpha - \nu/2 \end{matrix} \right. \right) \end{aligned} \quad (3.12)$$

valid under the conditions stated.

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REFERENCES

1. Bateman Ms. Project, *Integral transforms*, 1, (1954).
2. Bateman Ms. Project, *Integral transforms*, 2, (1954).
3. Bateman Ms. Project, *Higher trans. functions*, 1, (1953).
4. Bose, N. N., *Bull. Cal. Math. Soc.*, 42, 94-97 (1950).
5. MacRobert, T. M., *Quart. Journ. of Maths.*, 13, 65-70 (1942).
6. Varma, V. K., *Bull. Cal. Math. Soc.*, (communicated for publication).